

CHAPTER 3

SITE CHARACTERIZATION AND FEASIBILITY EVALUATIONS

3-1. Introduction. Prior to selecting MPE for implementation, the site characteristics and the nature and extent of contamination must be assessed to evaluate the feasibility of MPE. Data collection requirements for initial technology selection are presented at the beginning of this chapter, along with a suggested strategy for technology screening. Next, paragraphs 3-3 through 3-6 provide details on required pre-design site characterization parameters, including physical, chemical, and biological properties of site media and contaminants, and the corresponding data collection methods. Paragraph 3-7 presents a checklist of site characterization data requirements. Paragraph 3-8 describes remediation technology options. Finally, paragraph 3-9 provides guidance on performance of MPE feasibility studies.

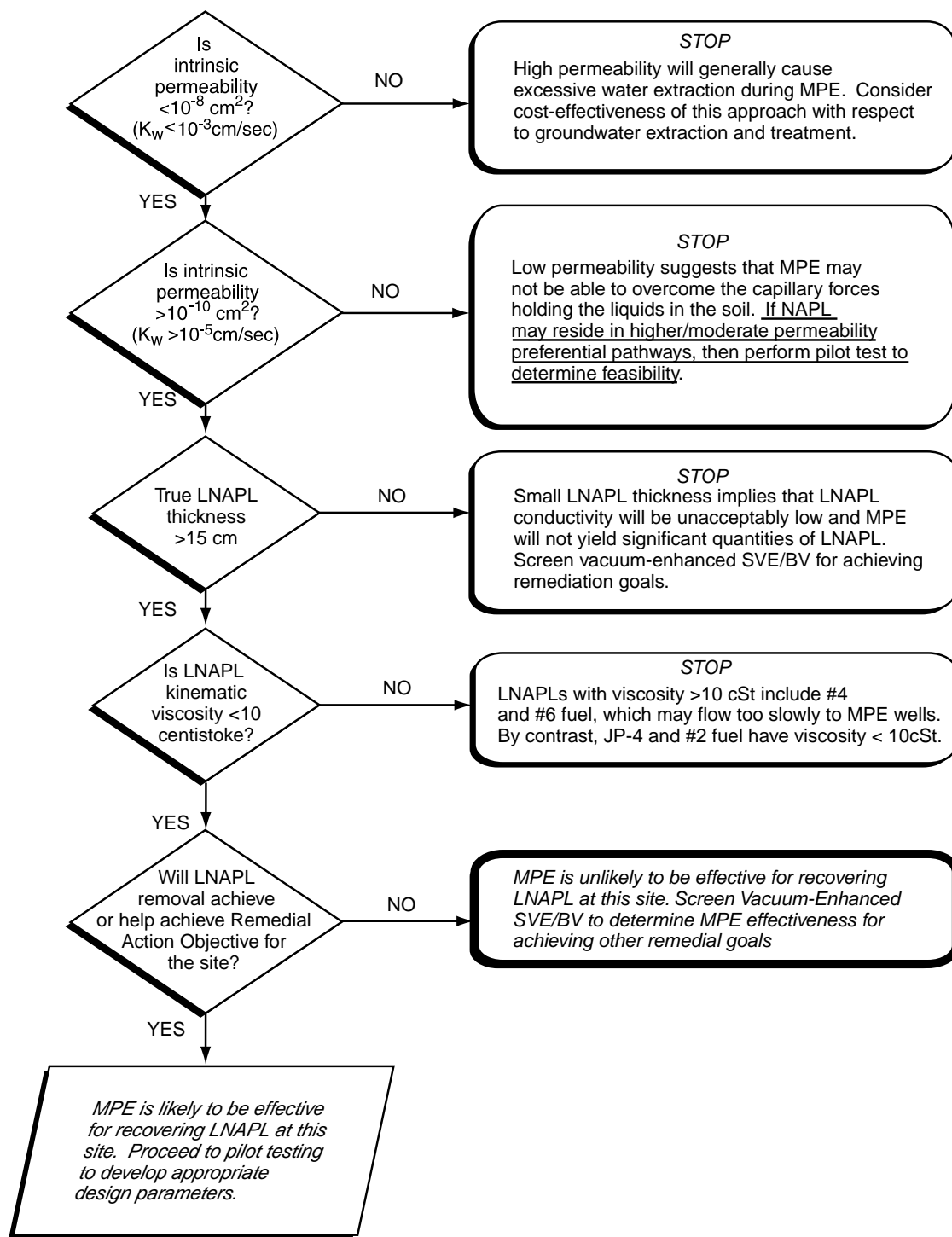
3-2. Data Collection Requirements for Technology Screening. It is advisable to perform technology screening as early in the process as possible, preferably concurrently with site characterization activities. Early evaluation of the data needs for remedy selection (and design) may reduce the need for subsequent mobilization to the field during design. However, it is usually inappropriate to collect detailed design data before a remedial alternative has been selected. Those undertaking technology screening must have a sense of the overall remedial objectives, some knowledge of the nature and extent of contaminants at the site, and a good grasp of the range of technologies available, including their limitations. Figure 3-1a is a technology screening matrix for LNAPL (free product) recovery using MPE, and Figure 3-1b is a technology screening matrix for vacuum-enhanced SVE/BV using MPE. Table 3-1 provides a checklist of site characterization data required for use of the two screening matrices for technology selection. An example format for a Sampling and Analysis Plan (SAP) is presented in [EM 200-1-3](#).

3-3. Site Conditions.

a. Identification of Site Features. Knowledge of pertinent above- and below-ground site features is necessary in the early stages of site characterization. This is typically performed by a site visit and records research.

(1) Surficial Topography. Surface topography and surface features can provide insight on subsurface conditions such as hydraulic gradient. Surface features, such as the condition of pavement, have a direct impact on the lateral extent of MPE influence.

(2) Surface Waters. Surface waters may provide information on water table location (e.g., wetland/swamp, gaining stream) and should be considered as a potential discharge location for system effluent water under a National Pollution Discharge Elimination System (NPDES) permit.



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Figure 3-1a. Technology Screening Matrix - Vacuum-Enhanced LNAPL (Free Product) Recovery.

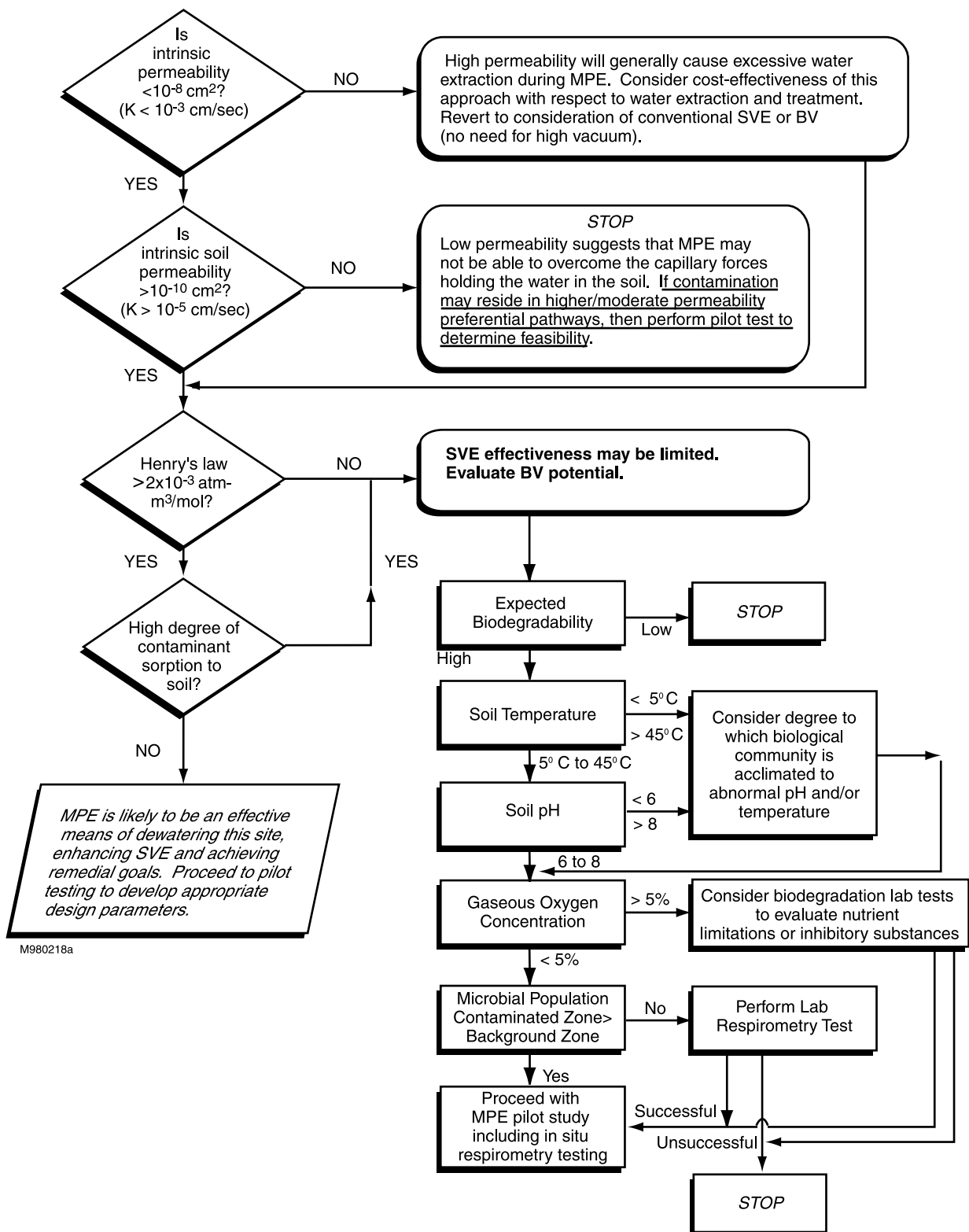


Figure 3-1b. Technology Screening Matrix - Vacuum-Enhanced SVE/BV (including vacuum dewatering).

TABLE 3-1
Checklist of Site Characterization Data Needs
for Technology Screening

Parameter	Source of Relevant Information (EM Paragraph No.)
Physical properties of soils: permeability, bulk density, moisture content, and capillary pressure-saturation curves	3-4 this EM; EM 1110-1-4005, Chapter 3
Stratigraphy, heterogeneity, and short-circuiting potential of formation	3-4 this EM; EM 1110-1-4005, Chapter 3
True versus apparent LNAPL thickness	3-5a(1) and 3-5a(2) this EM
NAPL viscosity, density, and interfacial tension	3-5a(7) this EM
Henry's law constants, boiling points, vapor pressures, and solubilities of contaminants, soil adsorption coefficients	EM 1110-1-4001, Chapter 2
Biodegradation potential	3-6 this EM; EM 1110-1-4005, Chapter 3
Soil/groundwater temperature	EM 1110-1-4005, Chapter 3
Soil/groundwater pH	EM 1110-1-4005, Chapter 3
Gaseous and dissolved oxygen concentration	3-5d(2)/3-5e this EM; EM 1110-1-4005, Chapter 3
Respirometry/microbial enumeration	3-6b/3-6c this EM; EM 1110-1-4005, Chapter 3

(3) Building/Basements. On-site buildings such as active facilities must be considered with respect to access restrictions and site security. Facility operating schedules may also affect operation of MPE systems (e.g., MPE system power supplied from the facility). Even at abandoned sites, existing foundations or former basements in close proximity to MPE wells can act as preferential pathways.

(4) Available Utilities. Availability of utilities must be checked in order to ensure compatibility of any equipment to be used with available power and water supply, etc. It is also important to ensure that utilities will not be subject to inadvertent disconnection by facility or security personnel.

(5) Utilities/Subsurface Interferences. Locating underground utilities must be done prior to any subsurface site work (typically by a utility locating service). On active installations, locating utilities should be coordinated with the base/facility electrician. Buried utilities may act as conduits for groundwater movement and preferential airflow pathways. As-built drawings (refer to paragraph 3-3a(9)) of buried utilities can be particularly useful, but may need to be supplemented by information obtained from experienced facility staff. Overhead obstacles such as power lines should also be identified as they may impact use of drill rigs at the site.

(6) Existing Wells. Existing monitoring wells may be useful as future MPE wells. Integrity of existing wells and suitability for MPE should be verified

prior to use (refer to paragraph 5-5d. Drinking water wells in the vicinity must be located, as system design may be required to prevent plume migration toward such wells.

(7) Unusual Features. Features such as surface soil stains which may be indicative of a former spill area; the presence of surface tanks or subsurface tanks which may be identified by aboveground vent pipes; areas of environmental stress; surface impoundments; and other potential sources of waste should be identified prior to MPE implementation.

(8) Verification of Site Boundaries. The property boundaries of the site should be identified to ensure that the remediation system will fit within the site and to identify possible off-site sources.

(9) Verification of As-Built Drawings. Pre-existing as-built drawings for the site can often be located in city or town property records and other archival locations. Caution should be exercised, however, when using these drawings because they may not be up to date. All drawings of the site furnished or obtained by others should be verified for accuracy in the field.

(10) Evaluation of Site Accessibility. Roadways to and from the site, entries onto the site, gates, and potential restrictions to site access should be identified.

b. Regulatory Context. An understanding of regulations driving remedial activities must be understood at any site. [Paragraph 9-2](#) provides more information on regulatory issues associated with MPE.

(1) Remedial Goals. Prior to implementation of any remedial activity, appropriate goals must be set. It is imperative that measurable and achievable criteria for meeting the goals are set in the cleanup criteria and/or Record of Decision (ROD) for the site. Once these criteria are established, the design and operation of the system should focus on attaining the remedial goals. In addition, it will be far easier to demonstrate that goals have been attained if plans for monitoring and confirmatory data collection are designed with the evaluation criteria in mind. Consideration must also be given to changing conditions (e.g., subsurface dewatering, changing plume) during MPE operation. Adjustment of system operation over time (e.g., lowering of the drop tube to draw down the water table exposing more of the affected subsurface soil to the applied vacuum) may also be required to meet the remedial goals.

(2) Receptors. All potential on- and off-site receptors such as residents, workers, wetlands, or nearby drinking water wells must be identified, as protecting these receptors may be the main objective of remediation.

(3) Points of Compliance. Points of compliance may be specified during the determination of remedial goals. It may be required that contaminant concentrations be reduced to remedial goals within a certain area surrounding the site or at certain downgradient locations. These requirements must be known prior to implementation of MPE and it must be determined whether the chosen technology is capable of meeting remedial goals at the points of compliance.

3-4. Physical Properties. Physical parameters that provide necessary information when characterizing a site for MPE are described in this section. Table 3-2 summarizes these and other pertinent parameters relative to soil.

TABLE 3-2

Soil Physical Parameters

Parameter	Sample Type	Analytical Method
Air-phase permeability (core scale)	In situ or undisturbed soil sample	Various ¹
Grain size distribution	Split spoon or other soil sample	ASTM D422
Total organic carbon	Split spoon or other soil sample	Lloyd Kahn, SW-846 9060
Porosity	Undisturbed 50 to 75 mm- diameter soil sample	Calculated from dry bulk density and particle density
Dry bulk density	Undisturbed 50 to 75 mm- diameter soil sample	ASTM D2850
Moisture content (of unsaturated zone soil)	Non-destructive field measurement; grab sample; or undisturbed 50- to 75-mm-diameter soil sample	Neutron access tube measurements (Gardner 1986); ASTM D2216
Soil moisture retention (capillary pressure-saturation curve)	Undisturbed 50- to 75-mm-diameter soil sample	ASTM D2325 ¹
Stratigraphy/heterogeneity	Soil borings	Visual observation; Breckenridge et al. 1991; USEPA 1991d; ASTM D2488; EM 1110-1-4000
Depth to groundwater and range of fluctuation; hydraulic gradient and flow direction	Water table monitoring wells	Water level meter or interface gauge and surveyed well elevations; ASTM D4750 (ensure that the probe weight is inert)
Hydraulic conductivity	Field Measurement	ASTM: D4043; D4044; D4050; D4104; D4105; D4106; D5269; and D5270
Notes: ¹ USACE Soil Vapor Extraction and Bioventing Engineer Manual (EM-1110-1-4001), November 30, 1995. Table Source: USACE In-Situ Air Sparging Engineer Manual (EM-1110-1-4005), September 15, 1997.		

a. Stratigraphy. Stratigraphy within the soils exposed to MPE must be understood prior to implementation. Soil stratigraphy should be observed continuously through collection of, for example, split-spoon soil samples throughout the depth interval of the MPE well. Variations in stratigraphy can dramatically favor the lateral flow of gas in permeable zones and impede the flow of gas through less permeable zones (e.g., clay lenses), potentially leaving a large volume of soil untreated (USEPA 1995). More information on determining stratigraphy can be found in USEPA (1991a), ASTM D 2488, and EM 1110-1-4001, Soil Vapor Extraction and Bioventing, Chapter 3.

b. Grain Size Distribution. Grain size distribution data should be obtained from soil samples collected within the screened interval of the MPE well. Care must be taken to obtain representative samples for grain size analysis as this parameter is measured on a small scale. Grain size distribution data will assist in specifying the well screens. It also can aid in evaluating the permeability of the soil, which is an important consideration in MPE, as very permeable soils are typically not suitable for TPE.

c. Porosity. Porosity is an important parameter to quantify for the treatment zone. The porosity value will assist in determining the permeability of the soil and is typically a required input parameter for fate and transport models. Porosity must also be estimated in order to analyze data used to determine hydraulic conductivity (e.g., distance-drawdown data).

d. Moisture Content. Moisture content can give designers confirmation of the location of the capillary fringe when samples are obtained directly above the water table (see Table 2-3 for approximate heights of the capillary fringe for various soil types). Although moisture content in soils near the water table may change with fluctuations in water table elevation, these data (when correlated with water table elevation) can help in locating the capillary fringe and smear zone.

e. Water Table Elevation. It is important to assemble all available site data regarding water table elevation when determining the feasibility of MPE or prior to design. Consideration must be given to seasonal fluctuations in the water table elevation because seasonal rise in elevation may cause the drop tube to become submerged and/or may "dead-head" certain vacuum pumps. Seasonal water table fluctuations also affect the recoverability of LNAPL. Although 1 atmosphere (10.3 m H₂O) is theoretically the maximum vertical distance over which suction can be used to lift a continuous column of water, due to pump inefficiencies and frictional losses in piping, the maximum attainable lift is approximately 9.1 m H₂O (Powers 1992). In applications where the water table elevation is below the elevation of attainable suction lift, DPE may be implemented using a submersible pump to remove liquid from the well. Alternatively, TPE can lift water from depths of as much as approximately 40 m when a sufficient air velocity is maintained to convey liquid droplets up the drop tube.

f. Hydraulic Gradient and Flow Direction. These parameters can effect placement of wells especially if the MPE system is used to control off-site plume migration. Seasonal changes in weather, surface infiltration characteristics, and tidal effects near large surface water bodies, can have temporal effects on hydraulic gradient and flow direction.

g. Vadose and Saturated Zone Pneumatic and Hydraulic Properties. Detailed information regarding these parameters is contained within existing USACE guidance. In particular, the reader should refer to [EM 1110-1-4001](#), Soil Vapor Extraction and Bioventing, Chapter 3; and [EM 1110-1-4005](#), In-Situ Air Sparging, Chapter 3.

(1) Permeability. As is the case with all in-situ remediation technologies that rely on inducing movement of fluid to accomplish mass transfer, MPE performance depends strongly on the permeability of the soil. It is therefore essential to evaluate the permeability of the zones targeted for MPE. Chapter 2 discussed the role that intrinsic and relative permeability play in the physics of multiphase flow in the subsurface. It is often useful to measure permeability on more than one scale, i.e., at the field scale through pumping tests, slug tests, and in situ air permeability tests; as well as in the laboratory through measurement of "intact" undisturbed soil cores. A program that combines two measurement scales, for example, such as a small number of slug tests or in-situ air permeability tests, and a larger number of core-scale measurements, offers the possibility of correlating the two. The correlation can allow extrapolation of values obtained using both scales at a few locations, to other more numerous locations where data are obtained only at the core scale (Baker et al. 1995; Baker and Groher 1998). Substantial areal and vertical variations in permeability/anisotropy can significantly affect MPE effectiveness because of their potential to focus fluid flow on some regions or

zones and in certain directions, while essentially by-passing others entirely. Examples of anisotropy may be seen from the difference between field-scale and laboratory-scale measurements. Field tests (e.g., pumping tests) tend to give results that show the dominant influence of horizontal permeability, while laboratory measurements within vertically-oriented soil cores reflect only vertical permeability. For this reason, the methodology in testing permeability must be known and taken into account when analyzing these data. As discussed above, the most useful results will most likely be obtained by evaluating both field- and laboratory-scale measurements. Applicable methods for measuring and estimating permeability are described in [EM 1110-1-4001](#), Soil Vapor Extraction and Bioventing, Chapter 3 and Appendix D, and [EM 1110-1-4005](#), In-Situ Air Sparging, Chapter 3.

(2) Groundwater Yield. Experience suggests that if a TPE well will produce a groundwater yield in excess of 20 L min^{-1} ($> 5 \text{ gpm}$) at a given level of applied vacuum, too much water will be extracted and the TPE well will tend to become flooded ([paragraph 2-5e\(5\)\(a\)](#)). It is generally preferable at such locations to use DPE.

(3) Capillary Pressure-Saturation Curves. Although it has not yet become a widespread practice, it can be extremely valuable to collect capillary pressure-saturation data on "intact" undisturbed soil cores. As discussed in Chapter 2, such data can be used to:

- Determine the air emergence pressure, i.e., the negative pressure (vacuum) that will need to be applied to saturated soil to initiate airflow (Baker and Groher 1998).
- Infer the effective thickness of the capillary fringe, within which air permeability $k_a=0$.
- Provide van Genuchten (1980) α and n parameters for use in determining true versus apparent product thickness ([paragraph 3-5a\(2\)](#)).
- Provide input parameters for multiphase flow modeling.

Applicable methods are specified in [EM 1110-1-4001](#), Chapter 3, and [EM 1110-1-4005](#), Chapter 3. Note that the "inflection pressure" (P_{infl}) described in the latter publication and in Baker and Groher (1998) is the same as the "air emergence pressure" (P_e) discussed herein.

(4) Thickness of Capillary Fringe. An additional parameter of great interest in the context of MPE is the vertical distance above the water table over which the soil is saturated, with capillary pressure $0 < P_c < P_e$, termed the effective thickness of the capillary fringe. This parameter can be determined through direct measurement of soil moisture content by collection of samples and gravimetric analysis, or through in situ measurements using a neutron probe, time domain reflectometry (TDR), capacitance probes or buried resistance blocks. Alternatively, this parameter can be obtained from capillary pressure-saturation curves ([paragraph 3-4g\(3\)](#)) or estimated from grain-size distribution data (Table 2-3). Applicable methods are specified in Table 3-2 (this EM), in [EM 1110-1-4001](#), Chapter 3, and [EM 1110-1-4005](#), Chapter 3.

h. Collection of Soil/Aquifer Samples. The physical properties described above can be defined with reasonable accuracy by a variety of invasive and

remote sampling methods including analysis of soil and groundwater samples, hydraulic testing, and surface and borehole geophysics. When using these data to assemble conceptual and quantitative models of site conditions, it is important to keep in mind the levels of uncertainty associated with each measurement. While some information such as water table elevations and hydraulic gradients can usually be determined quite accurately by straightforward measurements, other properties, such as hydraulic conductivity, can be measured in many different ways and can vary widely due to typical site heterogeneity, and different scales of measurement. Wherever possible, it is best to make many measurements, comparing results from different approaches and considering the limitations of the sampling and analysis methods employed. This is generally true of all site data, which are used to form the "conceptual model" of site conditions. An effort should be made to capitalize on the interrelatedness of the data. Collection of samples discussed in this section applies to both LNAPL and DNAPL except where noted. Additional guidance can be found in EM 200-1-3, Requirements for the Preparation of Sampling and Analysis Plans.

(1) Hazards of Invasive Characterization Methods.

(a) Installing borings or monitoring wells in areas of known or suspected DNAPL releases runs the risk of intersecting residual or mobile DNAPL during drilling, and potentially carrying contamination deeper into the subsurface. Commonly known as "short-circuiting," the problem is worst in the presence of thick accumulations of potentially mobile DNAPL, and is exacerbated by low viscosity and/or high density DNAPL. Short-circuiting may occur during drilling, along the open borehole, and/or after well completion, along the sandpack. In addition to spreading contamination, short-circuiting can also create difficulty in the interpretation of analytical results. To curb these hazards, non-invasive methods (e.g., geophysics and shallow soil gas surveys) may be used. However, non-invasive measures alone generally cannot provide enough detailed information to characterize a site. Where drilling is required over less invasive measures, or where known DNAPL source areas cannot be avoided, continuous soil cores should be collected and analyzed by visual inspection and gas analysis as drilling proceeds. Visual inspection can be aided by hydrophobic dyes (e.g., Sudan IV) and/or ultraviolet light. Typically, drilling is curtailed if DNAPL is reached. During drilling, high density drilling muds and high water pressures can be used to inhibit the entry of DNAPL into the borehole. Additionally, telescopic drilling may be used, in which successively smaller drilling casings are installed as the borehole proceeds downward. Ideally, each segment of casing is terminated in an aquitard. Thus DNAPL in upper layers cannot move down through the open boring or along the sandpack into lower layers. This method is slower and more costly than conventional drilling.

(b) To minimize the chance of short-circuiting, several precautions should be taken. These are included in the discussion of the investigation options below. A more focused discussion of specific DNAPL issues is given in paragraph 3-5b.

(2) Information from Borings and Excavations.

(a) Soil borings can provide soil samples and intact cores that can be visually inspected on-site and sent to a laboratory for measurement of physical properties. Excavations (test pits or trenches) offer the added advantage of direct in-situ observation of the sidewalls. Test pits can be excavated to depths of 3 to 5 m, depending on conditions, and afford a valuable view of important features such as vertical fractures and the lateral continuity of

fine grained layers. Visual inspection and grain size analysis help define stratigraphy, which provides a framework for the subsurface data.

(b) Alternately, small diameter direct-push drilling methods, while they still must be properly abandoned after sampling is completed, can be used to reduce the risk of short-circuiting (see paragraph 3-4h(1)(a)). When these methods are combined with continuous coring, field screening and on-site real time analysis, they provide a cost-effective and relatively safe approach to collect necessary data from DNAPL source areas and at sites in general. An example of this technology, Site Characterization and Analysis Penetrometer System (SCAPS), is described in Cone Penetrometer Site Characterization Technology Task Group (1996).

(3) Collection and Analysis of Intact Cores. Normal soil sampling methods (e.g., split-spoon sampling) often disturb the sample and thus change the sample's physical properties. Therefore, collection of undisturbed intact cores is necessary for accurate laboratory analysis of these parameters. Care should be taken in the process, since the extent to which intact cores are truly "undisturbed" is a point of debate. In addition to hydraulic conductivity and porosity, mentioned above, another class of important core data includes parameters associated with fractured bedrock and clay: fracture orientation, spacing, aperture, and secondary porosity. These data are necessary for characterizing flow in fractured media. However, the hazards of drilling in DNAPL zones are intensified by drilling in bedrock. The brittle and irregular nature of fractures can lead to unpredictable mobilization of DNAPL. Therefore, it is advised that an "outside-in" approach be applied when drilling in bedrock near suspected DNAPL zones.

(4) Geophysical Methods for Hydrogeologic Characterization. Surface and borehole geophysical methods provide useful, non-invasive tools for characterization of stratigraphy and permeable pathways in the subsurface. Methods include electromagnetic (EM) conductivity, electrical resistivity, neutron thermalization, ground-penetrating radar (GPR), and high-resolution seismic surveys. These methods can provide elevation contours of stratigraphic surfaces and the water table. Although borehole electrical methods and surface GPR have been shown to map DNAPL movement and distribution in ideal settings (Brewster et al. 1992), the ability of geophysics to detect DNAPL is still not clear (Pankow and Cherry 1996). Paragraph 3-5a(6) provides information on geophysical methods for contaminant detection.

3-5. Chemical/Contaminant Analyses.

a. LNAPL.

(1) Measurement Techniques for Apparent LNAPL Thickness.

(a) The thickness of LNAPL observed floating on groundwater in a well is termed "apparent thickness," to differentiate it from the "true thickness" which exists both above and below the water table in the surrounding formation. The relationship between apparent and true thickness is discussed below in paragraph 3-5a(2).

(b) The techniques available to measure the apparent thickness of LNAPL in wells include interface probes, hydrophobic tape, hydrocarbon detection paste on steel tape, transparent bailers, and other discrete depth samplers. With

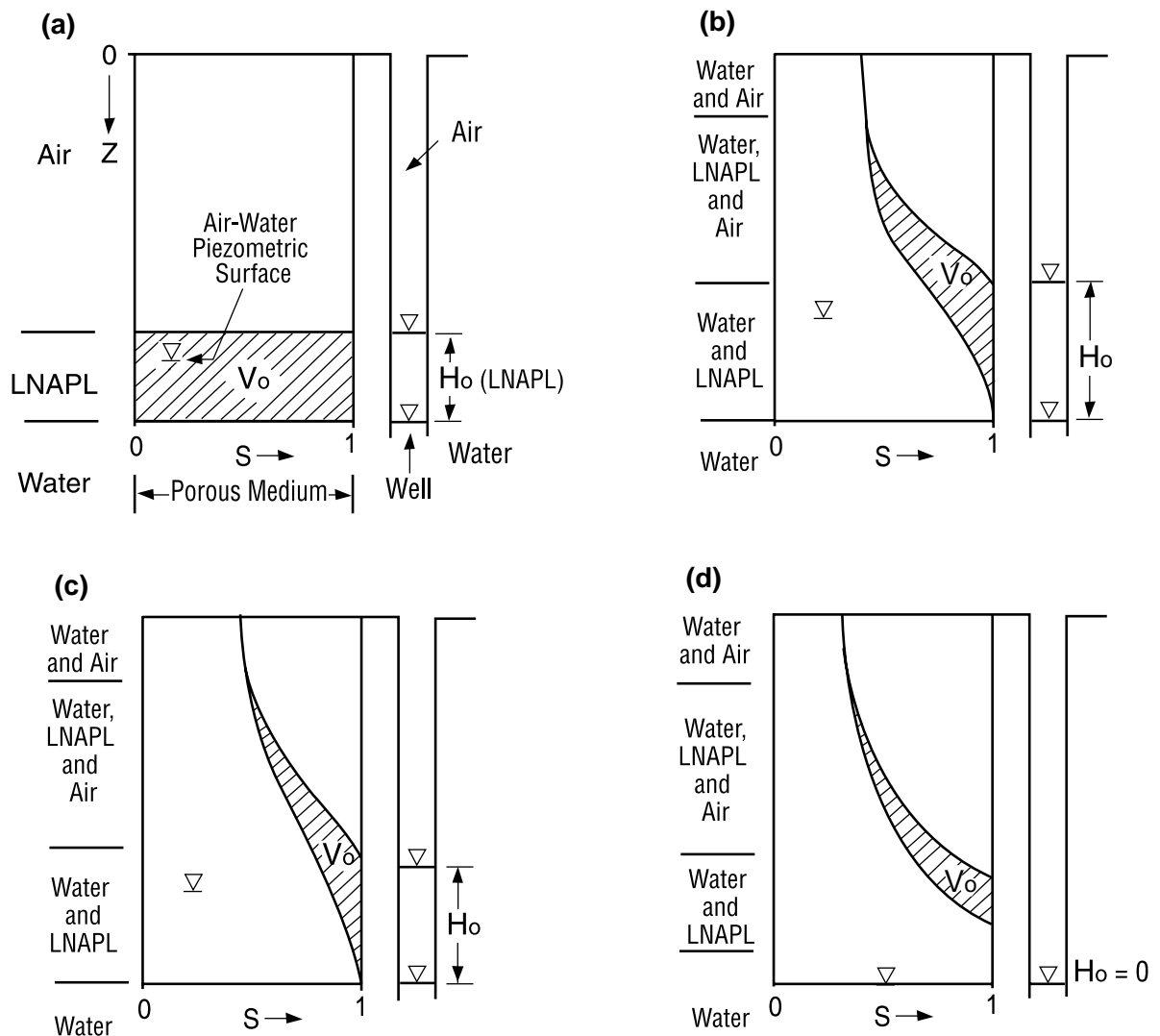
any of these methods, it is important that care be exercised to minimize disturbance of the liquid column during the measurement process. The interface probe is a device that uses optical and conductivity sensors to distinguish the air-liquid and LNAPL-water interfaces. Interface probes can be used to measure LNAPL and DNAPL thicknesses to within 0.3 to 3.0 cm (Mercer and Cohen 1990). Hydrophobic tape and hydrocarbon detection pastes show the top of the liquid level as a wet line and the LNAPL-water interface as a color change. This method is accurate to within 0.3 cm. Finally, transparent bottom-loading bailers may also be used to carry a sample to the surface for approximate measurement of LNAPL thickness. The bailer should be long enough so that its top is in air when the bottom is in water. To avoid overestimation due to LNAPL response while lowering the bailer, time should be allowed to attain hydrostatic equilibration while the bailer is lowered.

(2) Apparent Versus True LNAPL Thickness.

(a) At a site where LNAPL such as gasoline or diesel fuel is present in the subsurface, LNAPL is typically observed in wells screened across the water table and capillary fringe. All too often, however, LNAPL is viewed as occupying an oil-saturated "pancake" in the surrounding formation, the thickness of which is misconstrued as being linearly related to the thickness of the measurable LNAPL in the well. Although LNAPL reveals itself as a discrete oil lens floating on the water in a well, it does not occupy a distinct layer with a constant S_{or} floating on the top of the capillary fringe in the surrounding soil. For it to do so would violate the fundamental equations that describe the fluid pressure distributions in the porous medium and the monitoring well under conditions of static equilibrium (Farr et al. 1990). Nor is the apparent thickness, H_o (defined as the measurable thickness, at equilibrium, of the LNAPL lens in the monitoring well), equal to the true thickness, V_o (also known as the "hydrocarbon specific volume," defined as the actual hydrocarbon volume in excess of S_{or} per unit surface area of soil or aquifer) (Lenhard and Parker 1990; Newell et al. 1995). In addition, even in the absence of water table fluctuations, the upper and lower elevations of the oil lens floating in the well are not equal to the upper and lower elevations within which LNAPL is present within the soil. This elevation equivalency would hold only if the pores in the formation were all large, and the capillary forces and the S_{or} value thus infinitesimally small, as would be the case in a gravel deposit or a "delta function" soil (Figure 3-2a). Such a condition is rare in nature, and is thus not a realistic conceptualization.

(b) As we consider soils whose pore size distributions trend towards larger fractions of the smaller pore size classes, the magnitude of capillary forces increases, as does the degree to which the apparent thickness overestimates the true thickness (Lenhard and Parker 1990; Farr et al. 1990). The relative distributions of apparent versus true LNAPL thickness are represented in Figure 3-2b for a fine sand, and in Figure 3-2c for a silt loam. These USDA soil classifications would both fall roughly within the silty sand USCS classification category. (Note that an exact one-to-one correspondence between USDA and USCS soil classification categories cannot be provided.) Finally, Figure 3-2d depicts the case of a soil that exhibits a distinct h_{cne} (or P_a) value. No LNAPL will drain into a well from the soil if the LNAPL all exists at negative gage pressures such that $h_{cn} > h_{cne}$, which will be the case at $S_o < S_o(h_{cne})$; in this case, $H_o=0$ (Lenhard and Parker 1990; Farr et al. 1990). These authors present analytical methods enabling the prediction of V_o in homogeneous or stratified porous media based on the following data: a) site-specific measurements of H_o ; b) van Genuchten (1980) or Brooks and Corey (1966) $h_c(S)$ parameters, either i) fitted to moisture retention (air-water) data obtained from intact soil cores, or ii) estimated from grain size distribution data (Mishra et al. 1988; Lenhard and Parker 1990); and, c) ρ_o , σ_{ao} and σ_{ow} .

values obtained from measurements of a sample of the LNAPL or estimated from literature values.



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Figure 3-2. Relative vertical distribution of apparent LNAPL thickness, H_o , in a monitoring well versus true LNAPL thickness, V_o , at equilibrium, in: a) a delta function soil or clean gravel, $H_o = V_o$; b) a fine sand, $V_o \approx (0.005 \text{ to } 0.2)H_o$; c) a silt loam, $V_o \approx (0.005 \text{ to } 0.1)H_o$. V_o is typically a small fraction of H_o in soils; and d) in cases where the soil exhibits a discrete NAPL-water displacement pressure, no LNAPL will drain into the well if it at all exists at negative gage pressure. S = saturation. (After Farr et al. 1990; Lenhard and Parker 1990)

(c) Although the methods of Lenhard and Parker (1990) and Farr et al. (1990) are subject to a number of simplifying assumptions and uncertainties (Newell et al. 1995), a controlled study that compared the method of Lenhard and Parker (1990) to two more commonly applied but less physically well-founded approaches (De Pastovich et al. 1979; Hall et al. 1984) concluded that the method of Lenhard and Parker (1990) provided the best estimate of V_o . (Wickramanayake et al. 1991).

(d) It is important to note that for typical soils, V_o is often found to range from $<<0.01\%$ to 10% of H_o (Lenhard and Parker 1990; Farr et al. 1990; Baker and Bierschenk 1995). Such low ratios of V_o to H_o reflect the fact that most of the finer pores within the LNAPL zone tend to retain water, not LNAPL. Thus a reliance on apparent thickness can greatly overestimate the volume of mobile LNAPL in a formation.

(3) Recharge and Baildown Tests.

(a) Baildown tests have been frequently performed to estimate the oil content of the formation and spill volumes at sites where LNAPL is found floating on groundwater in wells. Similar to slug tests, which measure hydraulic conductivity of a formation, baildown tests involve quick removal of a volume of LNAPL, and subsequent observation of the liquid responses in the well. The reduced hydraulic head caused by the withdrawal of LNAPL from the well will induce LNAPL and water from the formation to enter and recharge the well. Both the water-LNAPL and LNAPL-air surfaces are measured and recorded over time.

(b) The use of baildown tests has begun to change, since physically-based models have been developed for estimating the oil content and spill volume based on the observed LNAPL thickness in the well and soil hydraulic properties (e.g., Lenhard and Parker 1990; paragraph 3-5a(2)). However, additional soil parameters are needed to carry out the calculation. While these can be obtained from undisturbed laboratory samples, estimates of formation oil content from baildown tests alone may offer qualitatively useful information as to the recoverability of free product, since the baildown test is conducted at field scale.

(4) Estimation of Volume of Recoverable Product. Once an estimate has been made of the true versus apparent LNAPL thickness for each location at which LNAPL has been measured in monitoring wells, a computer program such as OilVol (DAEM 1997) can be employed to estimate the volume of recoverable product at the site. In addition, the results of baildown tests can be used in a qualitative manner to indicate how readily recoverable the LNAPL is, which is itself a function of the "connectedness" of LNAPL-filled pores to the extraction wells or trenches at the field-scale. It is important to establish a good baseline estimate of the volume of recoverable product, because this will serve as a basis against which the progress of the remediation can be judged. Fluctuations in water table elevation will, of course, affect the recoverability of LNAPL and thus such benchmark values must be viewed as having a measure of uncertainty associated with them.

(5) Residual LNAPL.

(a) Unless spills occur on impermeable surfaces, LNAPL spills will generally sink into the subsurface and migrate downward until they reach either a low permeability layer or the water table. The degree of penetration depends on several factors, including volume and timing of the release, liquid properties, soil properties, and soil moisture profile. As LNAPL moves, it

leaves behind a "residual saturation," which is defined as the minimum content which a liquid has to attain in order to move in a porous medium (or alternatively the threshold below which it is no longer able to move) (De Pastrovich et al. 1979). The separate-phase liquid left behind, trapped by capillary forces, exists as disconnected blobs and ganglia, which continue to act as a source of contaminants that will dissolve into water and volatilize into soil gas. Residual saturation is the primary control on the penetration depth of a spill. The amount of liquid retained depends on the following factors:

- Media pore size distribution.
- Wettability (i.e., which liquid will preferentially occupy smallest pores; typically water is the wetting liquid with respect to air and LNAPL).
- Liquid viscosity and density ratios.
- Interfacial tension.
- Hydraulic gradients.
- Hysteresis.

(b) Because of the very small scale of many of the controlling factors (e.g., pore size distribution), and the very wide range of possible site conditions, it is impossible to directly predict residual saturations for a site. However, ranges of residual saturations for various LNAPL and soil types have been derived from laboratory studies. These ranges can be used to develop screening-level estimates. Table 3-3 gives estimated ranges of residual saturation in units of liters of LNAPL per cubic meter of soil, for different types of petroleum products and soils.

TABLE 3-3
Ranges of Residual LNAPL Concentrations in the Unsaturated Zone
(American Petroleum Institute 1993)

Medium	Gasoline (L/m ³)	Middle Distillates (L/m ³)	Fuel Oils (L/m ³)
Coarse gravel	2.5	5.0	10.0
Coarse sand and gravel	4.0	8.0	16.0
Medium to coarse sand	7.5	15.0	30.0
Fine to medium sand	12.5	25.0	50.0
Silt to fine sand	20.0	40.0	80.0

(c) After LNAPL reaches a low permeability layer or, more commonly, the water table, the LNAPL will spread out in what is often visualized as a "pancake." Fluctuations in water table elevation generally cause the LNAPL to also spread vertically in a "smear zone," leaving residual LNAPL in soil pores as it rises and falls with the water table surface. Time series measurements of water table elevation changes can provide estimates of the size of the smear zone. It is important to appreciate that the notion of a "pancake" is an oversimplification. Many of the pores within the "pancake" zone will retain water that will not be displaced by LNAPL. The finer-textured the soil, the more this will be the case.

(6) Geophysical Methods for Contaminant Detection. In general, geophysics can offer helpful supporting data for shallow LNAPL detection in dry soils. The geophysical method holding most promise is ground penetrating radar (GPR). GPR may be used to map hydrocarbons in the vadose zone. A strong contrast exists between the dielectric constant of liquid hydrocarbon and water in clean sands, gravel, and clayey or loamy soils. The authors indicate that GPR is able to delineate LNAPL pools and their migration. The critical prerequisite for GPR use appears to be low soil moisture content. Electromagnetic methods may also be used to locate gross contamination by variation in conductivity (USEPA 1993c). [Paragraph 3-4h\(4\)](#) provides a discussion of geophysical methods for hydrogeological characterization. Additional information on geophysical methods for contaminant detection can be found in *Subsurface Characterization and Monitoring Techniques - A Desk Reference Guide* (USEPA 1993c).

(7) Methods of Sampling and Analysis of LNAPL.

(a) Detection and sampling of LNAPL from extraction wells can be performed using an interface probe and Teflon[®] bailers or Teflon[®] strips. The use of Teflon[®] avoids potential contamination by phthalates which can interfere with the chemical composition analyses. The interface probe is lowered into the well to determine if LNAPL is present. If LNAPL is determined to be present, a disposable Teflon[®] bailer is lowered gently into the well and a sample is collected from the upper portion of the water table. If the LNAPL is visible in the bailer, the LNAPL will be transferred to (1) a 40 mL VOC vial with a Teflon[®]-lined hard cap (without a septum) for chemical composition analyses and (2) a 500 mL glass jar for density, viscosity, and interfacial tension analyses.

(b) If the LNAPL layer is not visible in the bailer or the interface probe does not detect LNAPL, then a Teflon[®] strip is lowered into the well, allowed to pass through the surface of the liquid in the well, and then drawn up through the surface and retrieved. The Teflon[®] strip can only be utilized to determine the chemical composition of the LNAPL, not the physical parameters. The Teflon[®] strip is placed in a wide-mouth glass jar and preserved with an appropriate volume of methanol and/or methylene chloride, depending on the analytes of interest. The volume should be enough that the Teflon[®] strip is fully immersed in the solvent. Preservation of the Teflon[®] strip must be performed in the field. In general, VOC analyses require methanol preservation, and SVOC and total petroleum hydrocarbon fingerprinting analyses require methylene chloride preservation. The resulting sample extracts must be shipped to the laboratory using applicable DOT regulations, which vary depending on the total volume to be shipped. Personnel handling the methanol and/or methylene chloride solvents should take proper precautions, including the use of protective gloves and safety glasses. Personnel should work with the solvents in a well-ventilated area to avoid inhalation. Methanol should also be stored away from extreme heat or other ignition sources due to its flammability.

(c) The analytical methods associated with the physical and chemical composition parameters of LNAPL are summarized in Table 3-4.

TABLE 3-4
LNAPL Physical and Compositional Analysis

Parameter	Analytical Method
Physical Parameters	
Density	ASTM D1475
Dynamic Viscosity	ASTM D88; D4243; D87; D1795
Interfacial Tension	ASTM D971; ASTM D2285; Lyman et al. 1982
Chemical Compositional Parameters	
Volatile Organic Compounds	SW-846 3585 or 5035/8260B (EPA 1986)
Semivolatile Organic Compounds	SW-846 3580/8270C (EPA 1986)
Total Petroleum Hydrocarbons	SW-846 3580/8015B (EPA 1986)

b. DNAPL. The presence of DNAPL presents unique challenges for MPE strategies. The reader is referred to Pankow and Cherry (1996) for a helpful discussion on DNAPL behavior and assessment. DNAPL behavior, particularly in terms of lateral occurrence and thickness, is radically different from that of LNAPL. LNAPL tends to form relatively even uniform layers, aided by the uniform water surface upon which it is spread. DNAPL "layers" on the other hand are typified by extremely heterogeneous distributions and unpredictable transport pathways. A small amount of DNAPL in the subsurface may be virtually impossible to locate and still lead to extensive and long-lasting dissolved plumes. An important consideration in evaluating the appropriateness of MPE strategies is the potential for significant DNAPL pool mobilization during dewatering operations. The wetting properties of DNAPL are generally such that DNAPL tends to "ball up" against water-saturated soils and spread out through air-saturated soils. DNAPL pools and blobs in a previously saturated aquifer that has been dewatered have the potential to begin spreading laterally, increasing the extent of contamination. Previously confined DNAPL can then find its way to weaknesses in an underlying confining layer and continue migrating downward to contaminate lower aquifers.

(1) Assessing the Presence of DNAPL. Paragraph 3-4h discussed DNAPL as it is associated with investigation techniques for defining physical properties in general. This section focuses on DNAPL as the object of investigation.

(a) Location of DNAPL source. Accurately locating a DNAPL source is difficult. The fact that DNAPL may exist in very fine stringers means that an extremely dense vertical and horizontal soil sampling network is generally required to find it. Minor variations in soil permeability can control DNAPL movement, shifting its location from where one might suspect it to be based on site records and other information. Furthermore, it has been shown that dissolved concentrations in wells can be quite low, even in close proximity to DNAPL pools, because of long intake screens with resulting dilution and lack of vertical delineation (Johnson and Pankow 1992).

(b) Dense vertical and horizontal profiling of groundwater plumes downgradient of suspected DNAPL source areas, combined with stratigraphic information and historical information on release locations, frequency and volumes can be used to develop effective conceptual models of DNAPL source zones (see [paragraph 3-5b\(1\)\(e\)](#)).

(c) Techniques to locate DNAPL. Initially, investigators should perform a thorough review of historical documentation, interviews, aerial photographs, and available site data. After this, the following techniques can be used in the field: observations during drilling, including visual evidence, enhanced visual evidence (ultraviolet fluorescence, hydrophobic dye), gas analyses, soil analyses, and drilling water analyses; soil gas surveys; observations of DNAPL in wells (quite rare); and geophysical methods (conditions permitting). In an experiment to test the ability to detect DNAPL, Cohen et al. (1992) demonstrated that enhanced visual evidence improved the positive identification of DNAPL from 30% (unaided visual observation) to over 80%. As mentioned in [paragraph 3-4h\(4\)](#), geophysical techniques may define hydrogeologic strata and locate likely candidate areas for DNAPL pooling, but the ability of these techniques to detect DNAPL itself is unproven. The often discontinuous presence of DNAPL in the subsurface makes it difficult even to come close enough to the DNAPL to use these techniques.

(d) Soil gas analysis of multi-component DNAPL. Soil gas sampling, generally from the upper 0.5 to 2.5 m of the soil column, may indicate the presence of DNAPL in the unsaturated zone. When analyzing gas concentrations as an indicator of DNAPL presence, it must be kept in mind that each individual component of a multi-component DNAPL, in accordance with Raoult's Law, will have a lower value than its gas concentration as estimated from its pure-phase vapor saturation. Although localized soil gas sampling can detect the presence of shallow residual DNAPL, the highly discontinuous nature of DNAPL occurrence and movement makes it likely that DNAPL will go undetected with typical gas survey sampling network spacings. Soil gas surveys can be appropriate for locating residual DNAPL provided the soil type and moisture content are considered when designing the survey. In principle, gases from SVE have the potential to reveal the presence of residual DNAPL, but this is likely to be an even less localized method than soil gas surveys.

(e) Dissolved plume delineation using monitoring wells and profiling. Although DNAPLs are referred to as "non-aqueous," their component compounds have solubilities which generally far exceed their Maximum Concentration Limits (MCLs) as set by USEPA or other regulatory agencies (see Table 3-5). Measurements of dissolved concentrations at a site can be used to infer DNAPL source areas. Because of the dangers of short-circuiting (see [paragraph 3-4h\(1\)](#)) in a suspected source area, it is advisable that investigations use an "outside-in" approach, where the emphasis is first placed on delineation of the dissolved plume, followed by investigation toward the source zone(s) (Pankow and Cherry 1996). This approach of defining the dissolved plume makes sense since it is the dissolved concentrations that generally pose the greatest risk to potential receptors. As a general rule of thumb, Newell and Ross (1991) suggest that concentrations near or above 1% of saturation (as expected based on component composition) are indicative of DNAPL. Table 3-5 shows solubility values for some pure chlorinated DNAPL compounds. Note that for a DNAPL composed of multiple chemicals, the effective aqueous solubility of a particular component can be approximated by multiplying the mole fraction of the chemical in the DNAPL by its pure phase solubility. This is analogous to Raoult's Law for vapor. The effective aqueous solubility can also be determined experimentally.

TABLE 3-5

**Pure Compound Solubilities at ~20°C for Selected Chlorinated Organic Solvents and Corresponding Maximum Concentration Limits (MCLs) for Drinking Water Set by USEPA.
(Pankow and Cherry 1996)**

Compound	Solubility (mg/L)	MCL (mg/L)
1,2-Dichloroethane	8,690	0.005
1,1,1-Trichloroethane	720	0.2
Carbon Tetrachloride	785	0.005
Methylene Chloride	20,000	0.01 ^a
Chloroform	8,200	0.1 ^a
Tetrachloroethene	200	0.005
Trichloroethene	1,100	0.005
^a New York State Department of Environmental Conservation Guidelines for Groundwater.		

(2) Assessing Mobility of DNAPL.

(a) Sampling and analysis of DNAPL. If DNAPL is detected and a reasonable amount (usually at least 10 cm³) can be extracted from a soil sample or from a well, it is helpful to send a sample to a laboratory for compositional analysis and for liquid properties: density, viscosity, and interfacial tension. Contact angle and wettability analyses may also be performed to obtain parameters used in more detailed calculations. Laboratory procedures for measuring these parameters are given in Cohen and Mercer (1993). The sample will generally be different than any original spilled mixture due to compositional changes that occur over time. Therefore, uncertainty in the composition needs to be taken into account in calculations, particularly those involving partitioning (paragraph 2-6b(3)). DNAPL samples may be collected from the bottom of a well using a pump, bottom-loading bailer, or discrete-depth canister, the latter usually giving the best results with limited sample disturbance. Analytical methods should follow high concentration protocols for use with DNAPL-contaminated soils and waters. It can be helpful to alert the laboratory about samples suspected of containing particularly high concentrations, such as obvious DNAPL material. The discontinuous nature of DNAPL occurrence tends to result in very wide ranges of possible constituent concentrations, however, and may make it difficult to predict contamination levels in a specific sample. It may be beneficial to perform on-site analyses of the DNAPL in order to anticipate concentrations.

(b) Depth of penetration of DNAPL. The depth of penetration of DNAPL into the unsaturated and saturated zones is controlled by physical properties of the DNAPL, the nature of the release, and geologic structure. Due to the very small scale of the controlling features, it is impossible to fully characterize a site and accurately predict the penetration depth for DNAPL releases. Still, it is important to understand the factors involved. In general, the following physical DNAPL properties favor deeper penetration: high density, low interfacial tension, and low viscosity. High aquifer permeability and vertical or sub-vertical geologic structure also favor greater depths of penetration. In a famous experiment, Poulsen and Kueper (1992) released 6 liters of PCE into

the sandy Borden Aquifer under two scenarios: an instantaneous spill (over a period of 90 seconds) and a slow drip (over a period of 100 minutes). The instantaneous spill penetrated 2.0 m and the slow drip penetrated 3.2 m (Figure 3-3). In both cases, careful excavation and analysis showed movement of the red-dyed PCE was strongly controlled by bedding structure in the sand. It moved preferentially along higher permeability layers following the bedding structure. Both spills exhibited significant lateral spreading due to small-scale bedding. The results demonstrate the wide variability involved in any estimate of penetration depth.

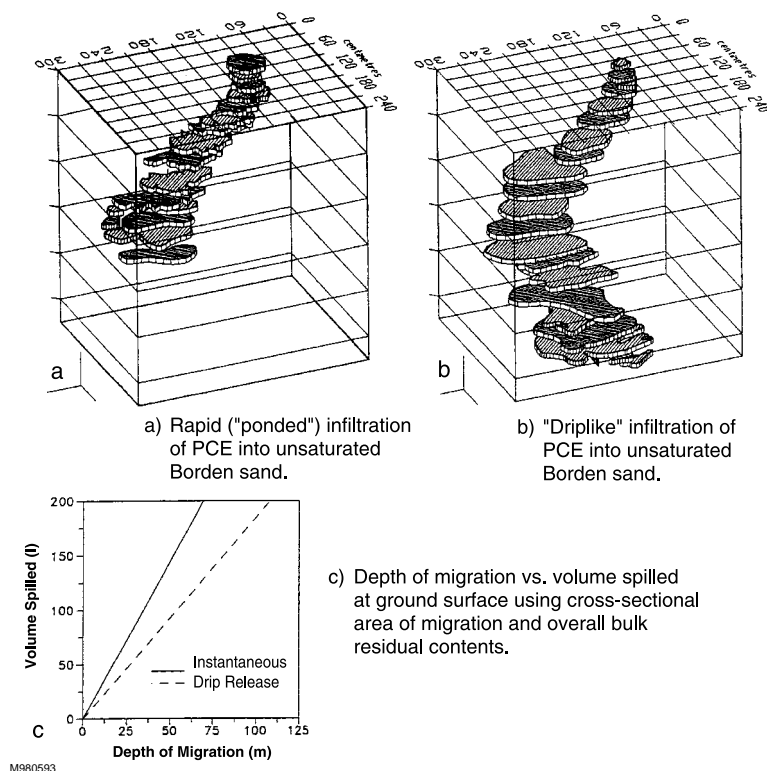


Figure 3-3. Results from Controlled Spill Experiments. (Poulson and Kueper 1992. Reprinted by permission of Environmental Science & Technology. Copyright 1992, American Chemical Society. All rights reserved.)

(c) Apparent versus true DNAPL thickness. In most cases where DNAPL is present at a site, it will probably not be found in wells. If it is found in wells, it is important to realize that the thickness found in the well will likely not reflect the true thickness in the formation. Several scenarios are possible, including those shown in Figure 3-4. As shown, entry pressures and relative differences in elevation between the screen and the DNAPL pool result in a variety of possible thicknesses in the well. Even where a well intersects a DNAPL pool, relative wetting against water and the pore properties of the well sand pack may prevent DNAPL from entering the well screen at all (Figure 3-4c). The true thickness of DNAPL will only be equal to the measured thickness in cases where the bottom of the well screen coincides exactly with the bottom of a large DNAPL pool and the pool is located in granular media in which it has displaced all of the water from the pores.

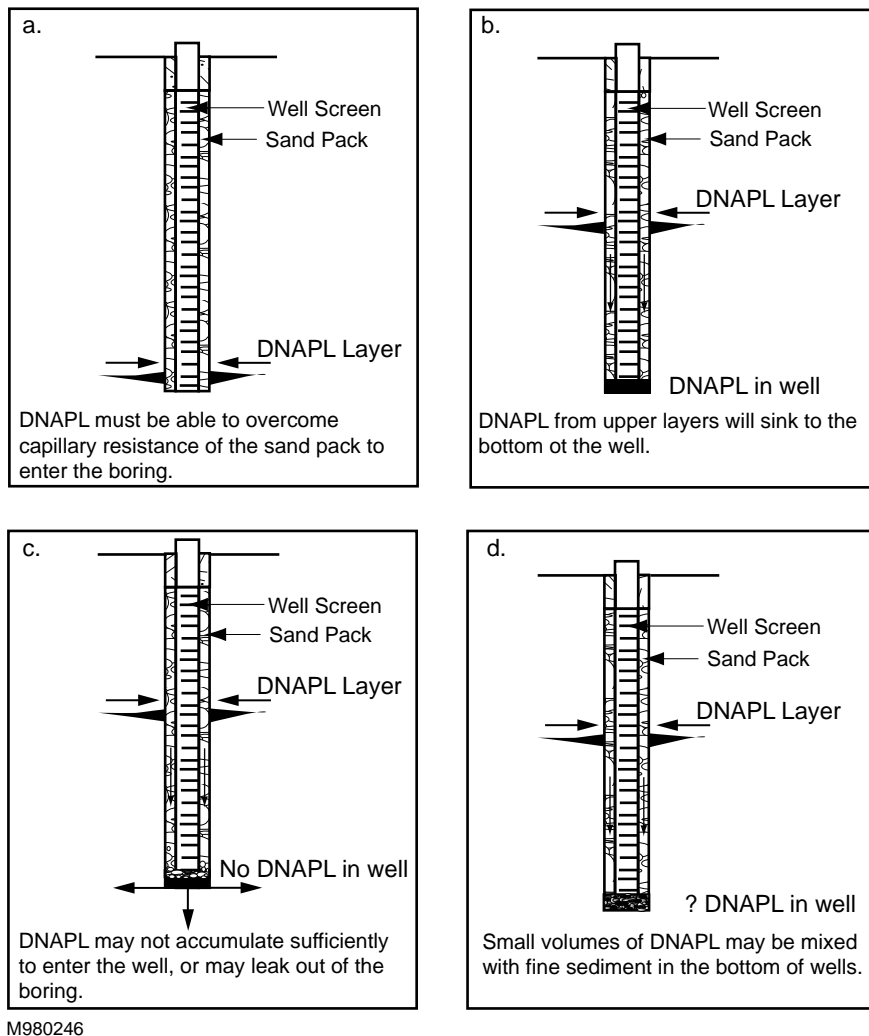


Figure 3-4. Various conditions under which DNAPL may accumulate and be identifiable in a monitoring well. (Pankow and Cherry 1996. Reprinted by permission of Waterloo Press. Copyright 1996. All rights reserved.)

(d) Importance of a confining layer during dewatering operations. DNAPL pools that have stabilized may be remobilized during dewatering operations. Changes in hydraulic gradients create pressure changes that can induce DNAPL movement. In addition, in an air-water-DNAPL setting, DNAPL will readily displace the air and directly imbibe into the dewatered portion of the formation. DNAPL will descend lower into the subsurface unless an adequate confining layer exists to impede vertical movement. It is therefore necessary to determine if a confining layer exists before dewatering.

(3) Residual DNAPL. As DNAPL migrates in a formation, residual DNAPL will generally remain in its wake, distributed as ganglia and blobs which will continue to dissolve into groundwater and vaporize into soil gas for extended periods of time. Also, DNAPL released into the subsurface will diffuse from fractures and higher permeability porous media into surrounding low permeability porous media (e.g., sedimentary rock matrix and silt and clay). Long after pool removal or other cleanup activities, the DNAPL locked in the formation pores will slowly diffuse back out into the primary groundwater flow pathways. Matrix diffusion and rate-limited mass transfer phenomena are the primary cause of the "tailing" typically observed in soil and groundwater remediation efforts and the elevated concentrations in groundwater that typically last decades or centuries (Parker et al. 1994). Downgradient containment is frequently used to address this dissolved plume. However, at some sites natural attenuation has been shown to be sufficient to alleviate risks to potential receptors.

c. Methods of Soil Sampling and Analysis.

(1) The development of sampling and analysis plans should be performed using the guidance document [EM 200-1-3](#), Requirements for the Preparation of Sampling and Analysis Plans.

(2) USEPA methods as well as USACE guidelines apply for the collection of soil samples (Table 3-6). [Paragraph 3-4h](#) should be referred to for a summary of soil sample collection methods. These methods are also discussed in [EM 1110-1-4005](#), In-Situ Air Sparging. Discussion of proposed soil sampling methods with regulators is also advisable.

TABLE 3-6

Soil Sampling: Preservation Requirements/Recommended Analytical Methods*

Chemical Parameter	Preservation	Analytical Method
Total Organic Carbon (TOC) or Fraction Organic Carbon (foc)	One 4 oz. clear glass jar; Cool, 4°C	Lloyd Kahn, SW-846 9060
Ammonia/Nitrogen ¹	One 4 oz. clear glass jar; Cool, 4°C	EPA 350.1-350.3; SM4500-NH ₃ A-H
Total Kjeldahl Nitrogen (TKN) ¹	One 4 oz. clear glass jar; Cool, 4°C	EPA 351.1-351.4; SM4500-N _{org} A-C
Nitrate/Nitrite-N ¹	One 4 oz. clear glass jar; Cool, 4°C	EPA 353.1-353.3, SM4500-N
Ortho-Phosphates ¹	One 4 oz. clear glass jar; Cool, 4°C	SM4500-P A-F
Total Phosphorus ¹	One 4 oz. clear glass jar; Cool, 4°C	EPA 365.4; SM4500-P A-F
PH	One 4 oz. clear glass jar; Cool, 4°C	SW-846 9045B, 9045C
Sulfate ¹	One 4 oz. clear glass jar; Cool, 4°C	SW-846 9035, 9036, 9038; EPA 375.1-375.4; SM4500-SO ₄ A-F
Sulfides ¹	One 4 oz. clear glass jar; Cool, 4°C	SW-846 9030A, 9031; EPA 376.1, 376.2; SM4500-S A-H
Moisture content	One 4 oz. clear glass jar; Cool, 4°C	EPA 160.1
Semivolatile Organic Compounds (SVOCs)	One 8 oz. clear glass jar; Cool, 4°C	SW-846 3540C or 3550B/8270C
Total Petroleum Hydrocarbons (TPH-extractables) ²	One 8 oz. clear glass jar; Cool, 4°C	SW-846 3540C or 3550B/8015B

TABLE 3-6 (Continued)

Chemical Parameter	Preservation	Analytical Method
Volatile Organic Compounds (VOCs) ³	Three methods: (1) Three 5g EnCore™ sampler; Cool, 4°C. (2) Two 40 mL VOA vials with 1 g sodium bisulfate and 5 mL water; add 5 g soil; Cool, 4°C. (3) One 40 mL VOA vials with 5-10 mL methanol; add 5 g soil; Cool, 4°C.	SW-846 5035 and 8260B
*Refer to appropriate state regulations for guidance.		
¹ Listed analytical methods are for aqueous samples and will need to be modified for soil samples.		
² Can be screened in the field using field screening kits (Petroflag, immunoassay kits) or via microextraction/GC-FID analysis		
³ Can be screened in the field using headspace methods along with (GC) and the appropriate detector (FID, PID, etc.)		
USEPA. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition including Final Update III, December 1997.		
USEPA. Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-200, March 1979.		
APHA-AWWA-WPCF. Standard Methods for the Examination of Water and Wastewater. 19th Edition, 1998.		
Kahn, L. 1988. Determination of Total Organic Carbon in Sediment. USEPA Region II, Edison, NJ.		

(3) Samples submitted for VOC analyses should be collected for low-level (acid solution preservation) and/or high-level (methanol preservation) analyses as described in SW-846 Method 5035. Other options are available for sample collection within SW-846 Method 5035 and may also be utilized for soil samples, if appropriate. Data quality objectives (DQOs [e.g. required detection limits]) may require the need for either low level or high level preservation procedures or may require preservation using both procedures, depending on the concentration ranges of VOCs in the soil samples. It may be beneficial to perform on-site analyses (e.g., using a field gas chromatograph [GC]) of the soil samples in order to determine whether the low level or high level method should be utilized. In general, low-level analyses should be utilized for VOC concentrations below 200 micrograms per kilogram ($\mu\text{g/kg}$); high level analyses should be utilized for VOC concentrations above 200 $\mu\text{g/kg}$. If any calibration ranges are exceeded during the low-level analysis, the high-level analysis also needs to be performed.

(4) The preservation procedures can be performed in the field or in the laboratory. If preservation is to be performed in the field, trained technical staff should be available due to the amount of chemicals utilized and the shipping regulations for these chemicals. In addition, the nature of the sample matrix, in cases of high carbonate content, may cause difficulty during the preservation of the samples in the acidic sodium bisulfate solution. In the event that technical staff are not available, the EnCore™ sampler (verified by the USACE Cold Regions Research and Engineering Laboratory), a disposable, volumetric, airtight sampling device (or equivalent), may be utilized for the collection of samples. A minimum of three EnCore™ samples (two for low level and one for high level analyses) should be collected per location in order to provide the laboratory with appropriate backup to accommodate the potential preservation problems or analytical problems which may occur. If quality control analyses (e.g., matrix spike/matrix spike

duplicated) are to be performed, additional EnCore™ samples will need to be collected.

(5) If samples are collected in the EnCore™ samplers, the laboratory must preserve the sample within 48 hours of sample collection and analyze the sample within 14 days of sample collection. Therefore, every attempt should be made to ship the EnCore™ sampler to the laboratory on the same day of sample collection for same day or overnight delivery. If the samples are preserved in the field, the laboratory must analyze the samples within 14 days of sample collection. Depending on the total volume of preservatives, the sodium bisulfate solution and the methanol may be U.S. Department of Transportation (DOT) Hazardous Materials and may therefore need to be shipped according to DOT shipping requirements. Depending on the project DQOs, the laboratory should perform the low-level and/or high-level preservation procedures.

(6) Solid samples also may contain high moisture content that may restrict the use of the EnCore™ sampler. If this occurs, preservation for low level and/or high level analyses (depending on DQOs) should be performed in the field.

(7) Whether the preservation occurs in the laboratory or in the field, the nature of the matrix, if high in carbonate content, may cause effervescence and thus, significant loss of VOCs, when preserved in the acidic sodium bisulfate solution. If significant effervescence occurs, the sample should be collected in an EnCore™ sampler. The laboratory should extrude the sample in water and analyze it within 48 hours of sample collection in order to minimize VOC losses.

(8) The options for sampling VOCs have been outlined above in the order that reduces VOC losses and ensures the most representative sample. Figures 3-5a and 3-5b present flow charts that summarize these options. In addition to reducing VOC losses, another objective of these flow charts is to make the sampling as simple as possible for the field team by trying to minimize the amount of chemicals utilized and/or shipped to and from the field. These flow charts should be used by both the field sampling team and the analytical laboratory.

d. Methods of Soil Gas Sampling and Analysis.

(1) The purposes of conducting soil gas surveys for MPE are similar to those discussed in [EM 1110-1-4005](#), In-Situ Air Sparging. Similarly, uses of the data collected from soil gas surveys, as well as their limitations, are discussed in [EM 1110-1-4001](#), Soil Vapor Extraction and Bioventing.

(2) Table 3-7 summarizes methods of soil gas collection. Sampling of soil gas for VOCs has been broken down into two categories, active and passive sampling. Active sampling involves driving a probe into the vadose (unsaturated) zone and drawing a vacuum to acquire a sample from the subsurface through the probe into a sample container or sorbent tube. The radius of influence will be dependent on the permeability of the soil formation. Passive sampling involves placing a sampler containing a sorbent with an affinity for the target analytes in the ground for a period of time. The target contaminants are collected by diffusion and adsorption processes.

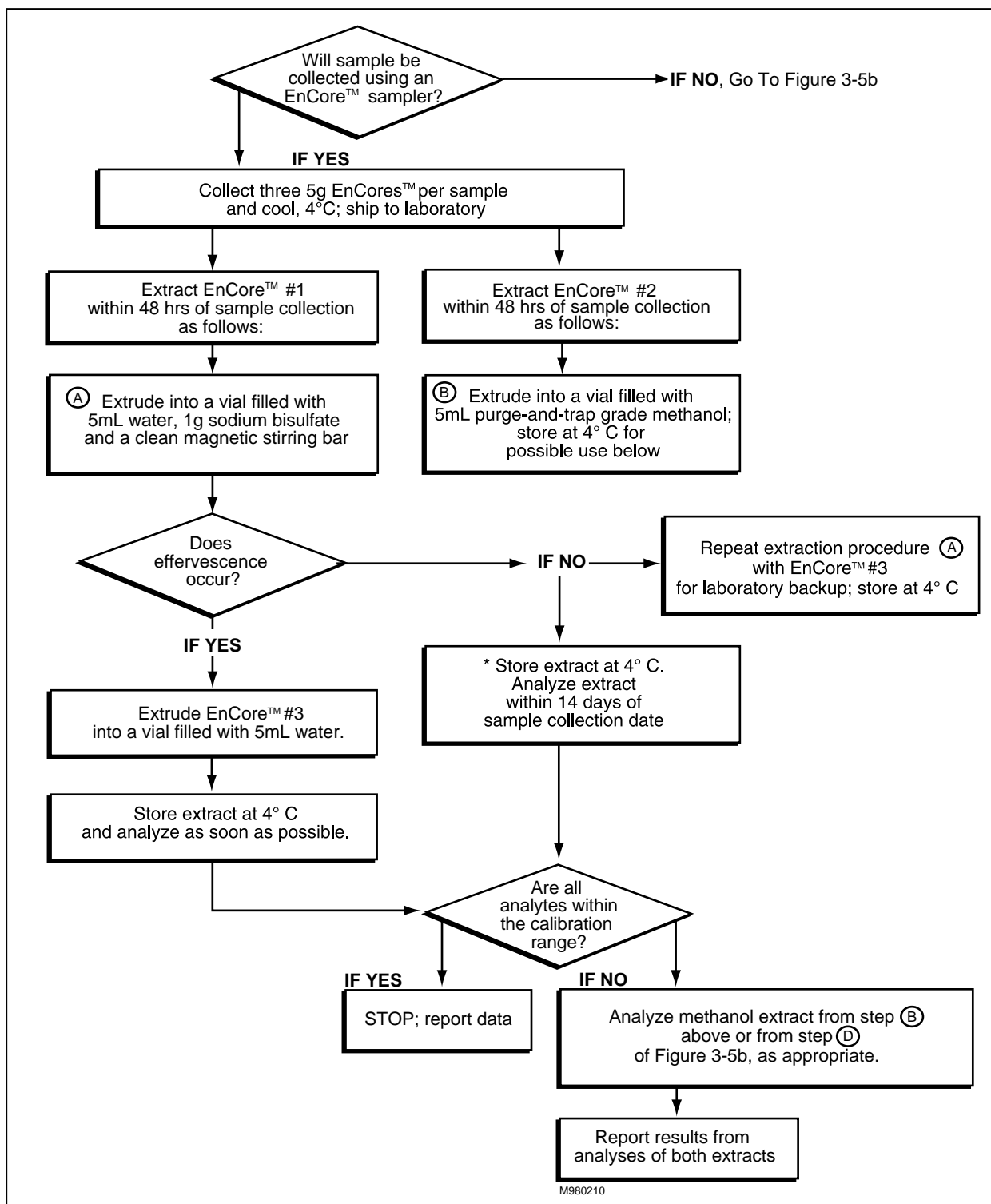


Figure 3-5a. VOC Sampling/Preservation Flow Chart. Use of EnCore™ or equivalent sampler is stipulated in Method SW846-5035.

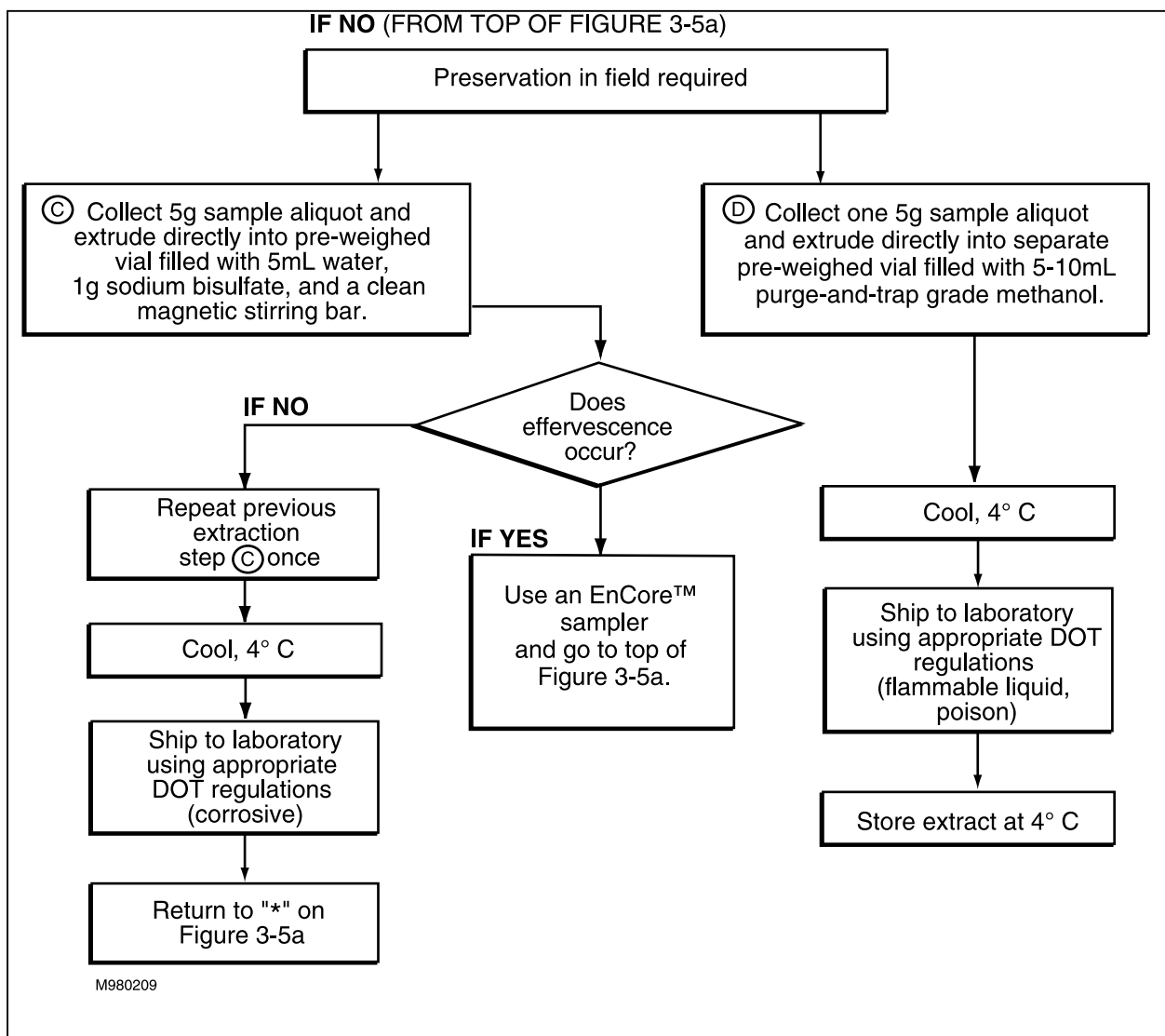


Figure 3-5b. VOC Sampling/Preservation Flow Chart. Use of EnCore™ or equivalent sampler is stipulated in Method SW846-5035.

TABLE 3-7

Soil Gas Sampling/Analytical Methods

I. VOLATILE ORGANIC COMPOUNDS (VOCs)	
A. Active Sampling	
Whole Air Collection Media Options	Sorbent Collection Media Options
Evacuated canisters Tedlar® bags Static-dilution glass bulbs Gas-tight syringes	Charcoal tubes Tenax® tubes Ambersorb® tubes Silica gel tubes Colorimetric detector tubes
Applicable Sampling and Analytical Method References: <ul style="list-style-type: none"> National Institute for Occupational Safety and Health (NIOSH) 1984. <i>Manual of Analytical Methods</i>. Third Edition. February 1984. USEPA 1987. <i>Compendium of Methods for the Determination of Toxic Compounds in Ambient Air</i>. EPA/600/4-84-041. USEPA 1988. <i>Field Screening Methods Catalog</i>. EPA/540/2-88-015. USEPA 1990. <i>Contract Laboratory Program - Statement of Work for Analysis of Ambient Air (Draft)</i>. American Society for Testing and Materials (ASTM) 1993. <i>Standard Guide for Soil Gas Monitoring in the Vadose Zone</i>. ASTM D 5314-93. 40 Code of Federal Regulations, Part 60, Method 18, 1997. USEPA, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition including final Update III, December 1997. 	
B. Passive Sampling	
Sample Collection Options:	
Gore-Sorber® modules Emflux® collectors	
Analysis: solvent extraction or thermal desorption followed by GC/MS analysis or analysis by GC equipped with the appropriate detector (FID, PID, ECD, etc.)	
Applicable References: <ul style="list-style-type: none"> Hewitt, A.D., <i>Establishing a Relationship Between Passive Soil Vapor and Grab Sample Techniques for Determining Volatile Organic Compounds</i>, US Army Corps of Engineers, September 1996. 	
II. OXYGEN, CARBON DIOXIDE, and METHANE	
Sample Collection and Analysis Options:	
In-situ collection with direct measurement using appropriate analyzer Active sampling: Tedlar® bags with measurement using appropriate analyzer	

(3) Active sampling can usually be accompanied by on-site analysis of air samples using GC techniques accompanied with the appropriate detector. Samples may be collected in Tedlar® bags, static-dilution glass bulbs, or gas-tight syringes. Colorimetric detector tubes also can be analyzed on-site. Active sampling into evacuated canisters or onto most sorbent tubes and passive

sampling usually requires more sophisticated analytical techniques (e.g., cryogenic trapping, purge-and-trap, solvent extraction, GC/mass spectrometry [GC/MS], etc.), which would not generally be appropriate for field use.

e. Methods of Groundwater Sampling and Analysis. Groundwater collection methods to be performed during the performance of MPE will be similar to those during IAS (EM 1110-1-4005). Table 3-8 summarizes container and preservation requirements for chemical analyses of groundwater samples. In addition, parameters that can be screened or analyzed in the field are flagged; field-screening options for these parameters are also listed.

TABLE 3-8
**Groundwater Sampling: Preservation Requirements/
Appropriate Analytical Methods**

Chemical Parameter	Preservation	Analytical Method
¹ Biological Oxygen Demand (BOD)	1 L polyethylene or glass bottle; Cool, 4°C	EPA 405.1; SM 5210 A-B
¹ Chemical Oxygen Demand (COD)	125 mL polyethylene or glass bottle; pH <2 with HCl or H ₂ SO ₄ ; Cool, 4°C	EPA 410.1-410.4; SM 5220 A-D
¹ Alkalinity	250 mL polyethylene or glass bottle; Cool, 4°C	EPA 310.1, 310.2; SM 2320 A-B
¹ Total Dissolved Solids (TDS)	250 mL polyethylene or glass bottle; Cool, 4°C	EPA 160.1; SM 2540C
Total Organic Carbon (TOC)	125 mL polyethylene or glass bottle; pH <2 with H ₂ SO ₄ ; Cool, 4°C	SW-846 9060; EPA 415.1, 415.2; SM 5310 A-D
¹ Iron (total and field filtered) [†]	1 L polyethylene or glass bottle; pH <2 with HNO ₃ ; Cool, 4°C	SW-846 6010B
Calcium, Magnesium, Manganese, Sodium, Potassium	1 L polyethylene or glass bottle; pH <2 with HNO ₃ ; Cool, 4°C	SW-846 6010B
¹ Ammonia-Nitrogen	500 mL polyethylene or glass bottle; pH <2 with H ₂ SO ₄ ; Cool, 4°C	EPA 350.1-350.3; SM 4500-NH ₃ A-H
Total Kjeldahl Nitrogen (TKN)	500 mL polyethylene or glass bottle; pH <2 with H ₂ SO ₄ ; Cool, 4°C	EPA 351.1-351.4; SM 4500
¹ Nitrate/Nitrite	250 mL polyethylene or glass bottle; pH <2 with H ₂ SO ₄ ; Cool, 4°C	EPA 353.1-353.3; SM 4500
¹ Sulfate	250 mL polyethylene or glass bottle; Cool, 4°C	SW-846 9035, 9036, 9038; EPA 375.1-375.4; SM 4500-SO ₄ A-F
¹ Sulfide	1 L polyethylene or glass bottle; pH >12 with NaOH; 4 drops 2N Zinc Acetate/liter; Cool, 4°C	SW-846 9030B, 9031; EPA 376.1, 376.2; SM 4500-S A-H
^{1,2} pH [†]	100 mL polyethylene or glass bottle	SW-846 9040A, 9040B; EPA 150.1, 150.2; SM 4500-H ⁺ A-B
² Temperature [†]	1 L polyethylene or glass bottle	EPA 170.1; SM 2550 A-B
^{1,2} Dissolved oxygen [†]	300 mL BOD bottle; 2 mL MnSO ₄ ; keep in dark	SM 4500-O A-G
	300 mL BOD bottle	EPA 360.1
	300 mL BOD bottle; 2 mL MnSO ₄ ; 2 mL alkaline iodide azide; keep in dark	EPA 360.2
² Conductivity [†]	1 L polyethylene or glass bottle; Cool, 4°C	SW-846 9050A; SM 2510 A-B
² Redox potential (ORP) [†]	100 mL polyethylene or glass bottle	SM 2580 A-B
¹ Hardness	250 mL polyethylene or glass bottle; pH <2 with HNO ₃	EPA 130.1, 130.2; SM 2340 A-C
¹ Phosphorus (total)	100 mL glass bottle; pH <2 with H ₂ SO ₄ ; Cool, 4°C	EPA 365.4

TABLE 3-8 (Continued)

Chemical Parameter	Preservation	Analytical Method
¹ Orthophosphates (filtered in field)	100 mL glass bottle; add 40 mg HgCl ₂ /liter; freeze, -10°C	SM 4500-P A-F
¹ Chlorides	125 mL polyethylene or glass bottle	SW-846 9250, 9251, 9253; EPA 325.1-325.3; SM 4500-Cl A-F
Depth to free NAPL phase	Direct push "soil boring", e.g., cone penetrometer	Laser Induced Fluorescence
³ Volatile Organic Compounds (VOCs)	Three 40 mL VOA vials; pH <2 with HCl; no headspace; Cool, 4°C	SW-846 5830B/8260B
Semivolatile Organic Compounds (SVOCs)	Two 1 L amber glass bottles; Cool, 4°C	SW-846 3510C or 3520C/8270C
⁴ Total Petroleum Hydrocarbons (TPH-extractables)	Two 1 L amber glass bottles; Cool, 4°C	SW-846 3510C or 3520C/8015B
¹ Can be determined in the field using CHEMETRIC or HACH field test kits (colorimetric or titrimetric methods); no preservative needed for field tests. ² Can be determined in the field using the appropriate field instruments (e.g. pH meter, conductance meter, etc.). ³ Can be screened in the field using headspace methods along with (GC) and the appropriate detector (FID, PID, etc.) or using the SCAPS HydroSparge VOC sensing system (see other USACE guidance). ⁴ Can be screened in the field using immunoassay test kits or via microextraction/GC-FID analysis. [†] It is strongly recommended that these parameters be analyzed in the field.		

(1) Direct-Push Methods. In unconsolidated material, it is often possible to use direct-push (also called drive point) methods. A short intake screen connected to tubing or pipe is fitted with a conical end piece and is pushed into the ground using drill rods. The short intake (typically 0.3 or 0.6 m) makes it unlikely that DNAPL will be intercepted. It is still possible that short-circuiting will occur along the sides of the piping. Direct-push methods are usually faster and cheaper than completed wells and therefore they can provide greater sampling coverage for soils loose enough to allow their installation. Groundwater samples can be taken over several discrete depth intervals along a "profiling line" to provide a detailed profile of a plume. The idea is that the profiling line is oriented to form a vertical plane of data points slicing through the dissolved plume. Although drive points are very useful, one potential difficulty is that in very fine-grained soils the small intake screens can become clogged with silt over longer periods.

f. Considerations Common to Chemical Analysis of Soil, Soil Gas, and Groundwater Samples.

(1) Recommended Analytical Methods. Table 3-9 summarizes the chemical parameters of interest and the reasons for analysis of these parameters. Additional chemical parameters may be necessary based upon project-specific contaminants or DQOs. It should be noted that samples (soil, soil gas, or groundwater) submitted for GC/MS analyses of target VOCs or SVOCs may occasionally exhibit the presence of unknown compounds. As opposed to GC analyses, the GC/MS technique allows for the potential identification of the unknown peak. This is done by performing a library search of the peak in question. The library search program compares the spectrum of the unknown peak to a library of mass spectra to find a match. Since the mass spectra in the library were produced under different instrumental conditions than the unknown peak, the identification is considered tentative and the unknown compounds are therefore referred to as Tentatively Identified Compounds (TICs). In some

instances, the spectrum of an unknown peak may yield a similar pattern to more than one compound. In this case, it is more appropriate to report the TIC as a chemical class (e.g., unknown alkane, alkyl-substituted benzene). The reported concentrations of TICs are estimated values since these compounds were not calibrated for by the laboratory. It is imperative to instruct the laboratory to identify these TICs in samples known to be contaminated early in the site characterization. Once identified, the laboratory can prepare to calibrate for these compounds for future site assessment programs, which would allow for accurate identification and quantification.

(a) Comprehensive listing of analytical methods. Methods for analysis of potential chemical parameters associated with soil, soil gas, or aqueous samples are summarized in Tables 3-7, 3-8, and 3-9.

TABLE 3-9

Chemical Parameter/Purpose of Analysis

Chemical Parameter	Purpose
BOD	to indicate the quantity of biologically oxidizable material (i.e., electron donors) present; to determine if the BOD level in extracted water will meet the discharge requirement, if applicable
COD	to indicate the quantity of chemically oxidizable material present; to assess the availability of electron donors
Alkalinity	to determine whether conditions are too acidic or alkaline to support abundant microbial populations and whether or not CO ₂ will be generated as a result of aerobic degradation
TDS	to determine salinity
TOC	to indicate ability of organic compounds to partition to the solid or aqueous phases; may be used to assess availability of electron donors
Iron (total and field filtered)	to indicate presence of either reductive or oxidative conditions and to indicate need for treatment of iron in extracted groundwater; ferrous iron may be used to assess whether ferric iron is being used as an electron acceptor
Calcium, Magnesium, Manganese, Sodium, Potassium	to determine presence of cations/anions which could precipitate in any treatment processes
Ammonia-Nitrogen	to determine nitrogen which is readily available to microorganisms
TKN	to determine total pool of organic nitrogen plus ammonia (includes less available nitrogen)
Nitrate/Nitrite	to indicate level of available nitrogen and presence of oxidative conditions; may be used to assess the availability of nitrate as an electron acceptor
Sulfate	to indicate whether subsurface conditions tend to be reductive or oxidative; may be used to assess the availability of sulfate as an electron acceptor
Sulfide	to indicate whether subsurface conditions tend to be reductive or oxidative; may be used to assess whether sulfate is being used as an electron acceptor

TABLE 3-9 (Continued)

Chemical Parameter	Purpose
pH	to determine whether conditions are too acidic or alkaline to support abundant microbial populations and whether or not CO ₂ will be generated as a result of aerobic degradation
Temperature	Important because many physical, chemical and biological properties and processes are temperature dependent.
Dissolved oxygen	to determine whether aqueous conditions tend to be aerobic or anaerobic and the extent to which these conditions vary with depth and location
Conductivity	to indicate salinity and electrolyte content
Redox potential (Eh)	to determine whether aqueous conditions tend to be aerobic or anaerobic and the extent to which they vary with depth
Hardness	to indicate alkalinity and tendency for scale formation
Phosphorus (total)	to indicate levels of all forms of phosphorus
Orthophosphates (filtered in field)	to indicate levels of readily available phosphorous
Chlorides	to determine presence of anions which may indicate dechlorination
Depth to free NAPL phase	to determine appropriateness and progress of remediation technique
VOCs (soil gas)	to estimate the initial concentration in the MPE gas emissions; to locate the soil contamination and guide the placement of MPE wells
VOCs (soil and groundwater)	to assess presence and concentration of target VOCs and associated chemicals; to determine appropriate remediation technique
SVOCs	to assess presence and concentration of target SVOCs and associated chemicals; to determine appropriate remediation technique
TPH- extractables	to assess presence and concentration of TPH and determine type of petroleum product present; to determine appropriate remediation technique

(b) Screening methods. Tables 3-7, 3-8, and 3-9 also highlight chemical parameters that can be analyzed on-site. Generalized technologies are provided for these on-site analyses.

(2) Estimation of Total Contaminant Mass.

(a) When selecting the appropriate remediation technology for the site, it is important to consider not just the concentrations of contaminant, but the total mass of contaminant present in the subsurface. Measured concentrations of dissolved contaminants have often been the focus of remedial investigations and are often the regulatory measure by which a site is deemed "clean" or "dirty." However, dissolved phase contamination may be only a small fraction of the total mass of contamination present at a given site. To achieve remediation goals, it may be necessary to remove contaminant mass that is dissolved, adsorbed onto soil, or present as a separate, non-aqueous phase.

(b) Dissolved contaminants are often in equilibrium with contaminants sorbed to the soil matrix. Removal of dissolved phase contamination via MPE may result in relatively clean water being drawn into the treatment zone and subsequently becoming contaminated by adsorbed contaminants re-equilibrating with the "new" pore water. Similarly, groundwater that comes into contact during MPE with NAPL will become contaminated. Thus it is critical to account for all of the contaminant mass and the various subsurface "compartments" where the mass may reside (adsorbed, NAPL, aqueous-phase, and gas-phase). Once the fraction of mass of contaminant residing in the various subsurface compartments is understood, then the remediation strategy can be developed.

(3) Cross-Media Correlations. The relationship of chemical compounds detected with soil analyses, and those detected by soil gas and groundwater analyses, is as discussed with respect to SVE/BV and IAS processes (EM1110-1-4001 and EM1110-1-4005).

3-6. Evaluation of Biological Degradation Potential.

a. Factors Influencing Biodegradation During MPE. One of the potentially important mechanisms for in situ treatment of contaminants during MPE is biotransformation. The paragraphs that follow discuss considerations useful in the evaluation of biodegradation and its applicability to a given site.

(1) As with all in situ remediation approaches, the potential for organic contaminant removal by microbial degradation during MPE is dependent on a variety of site specific factors, including:

(a) Amenability of contaminants to biodegradation. In general, every organic compound has an intrinsic potential for biodegradation by soil microorganisms. This potential may be governed by intrinsic parameters such as the structure of the molecule or its water solubility.

(b) Presence of microorganisms acclimated to the site contaminants. Soil may contain as many as 10^8 colony forming units (CFU) microorganisms per gram of soil, often representing a large variety of organisms. Years of exposure to environmental contaminants can influence the makeup of the microbial population, by providing a substrate or food source for a particular segment of the population. Over time, the microbial population becomes acclimated to the anthropogenically contaminated environment.

(c) Presence of toxic or inhibitory constituents (organic and inorganic). Sometimes, though not often, soil may contain compounds or elements to which the microbial population has not or can not acclimate. It is very difficult to determine *a priori* whether toxic or inhibitory constituents are present in site soil. There are no specific criteria established against which soil analytical data can be compared to identify inhibitory substances. Inhibition may be observed directly during respirometry testing or indirectly through microbial enumeration (discussed below), and the cause of the inhibition may be deduced. However, the same process that enables the microbial population to acclimate to the contaminants of concern often enables the population to acclimate to potential inhibitors.

(d) Availability of oxygen (or other electron acceptors). Microorganisms can use many environmental contaminants as substrates or electron donors, and thus transform the contaminant, often to a less toxic compound. Oxygen is a common electron acceptor for such biotransformations. The potential for biodegradation of contaminants during MPE is dependent on the ability of the MPE system to deliver oxygen proximate to the contamination. This, in turn, is

a function of the permeability of the soil. MPE will primarily affect the oxygen content of the soil gas and pore water in the vadose zone, and will have minimal affect on the saturated zone, other than possibly drawing oxygen-rich, uncontaminated groundwater toward the MPE well(s). (Some compounds, notably chlorinated ethenes, are themselves used as electron acceptors under anoxic [very low oxygen] conditions. Soil aeration by MPE will not significantly promote biodegradation of these compounds.)

(e) Other chemical environmental factors. Key factors for determining the potential of contaminant biodegradation are the availability of nutrients and suitable pH in the proximity of the contamination. There are a variety of nutrients such as nitrogen (N) and phosphorus (P), in addition to substrate/contaminant and electron acceptor (typically oxygen), that are necessary for microbial metabolism. Without these nutrients, biodegradation may not occur during MPE. Similarly, soil that has a pH that is unusually high (>11) or low (<3) may not support biodegradation during MPE. Optimal soil pH is generally in the range of about 6 to 8. It is important to note, however, that the tendency of soil microbial populations to acclimate to their environment makes it difficult to identify absolute levels of nutrients or pH that are required to support biodegradation in soil.

(2) The potential contribution of biodegradation for removal of contaminant mass during MPE is dependent on the same physical parameters as SVE (e.g., contaminant solubility, soil permeability, foc, and soil homogeneity), except the contaminants' volatility. Contaminants that are amenable to biodegradation, but not volatile enough to be extracted by MPE (e.g., naphthalene), may be removed by biodegradation promoted by MPE through soil aeration. Therefore, evaluation of biological degradation potential during MPE intended to promote biodegradation requires the same assessment of physical-chemical parameters as for MPE that is primarily intended to promote mass removal by extraction, with additional assessment of the factors described above.

(3) The contribution of biodegradation to mass removal during MPE is primarily relevant to compounds that are readily biodegradable under aerobic conditions, such as low and moderate molecular weight hydrocarbons found in petroleum fuels (e.g., gasoline, kerosene, JP-4, and diesel fuel). This is due to two factors: (1) the electron acceptor provided during MPE is oxygen which creates aerobic conditions in the treatment area; and (2) petroleum constituents are much more amenable to aerobic biodegradation than DNAPL constituents such as most chlorinated solvents. Subsurface aeration does not typically promote biodegradation of chlorinated solvents that are not amenable to biodegradation under aerobic conditions. An exception to this rule is aerobic co-metabolic biodegradation of some chlorinated ethenes. Some microorganisms, such as methanotrophs and propanotrophs (methane and propane utilizing) microorganisms, as well as toluene degraders can biodegrade compounds such as TCE, DCE, and VC in the presence of oxygen co-metabolically (i.e., using the enzymes normally used to metabolize their primary substrate). Since co-metabolism of these compounds does not provide energy for the microorganisms, suitable concentrations of primary substrate must be present (at least intermittently) to support biodegradation of the chlorinated ethenes. In the case of methanotrophic biodegradation, methane is often present in soil gas in anaerobic soil conditions. High rates of vacuum extraction often experienced during MPE may deplete the methane from the subsurface before significant contaminant biodegradation occurs. Also, by aerating the soil, the anaerobic conditions that generate methane are shut down. In contrast, when toluene is co-located with these chlorinated ethenes (e.g., when fuel and chlorinated solvents have been spilled at the same site), then aeration due to MPE may promote co-metabolic biodegradation of the chlorinated ethene(s). The rate of degradation will generally be low, but may be significant.

(4) Discussions of biological degradation potential and important microbiological and environmental factors can be found in [EM 1110-1-4001](#), Soil Vapor Extraction and Bioventing, Chapter 3, and [EM 1110-1-4005](#), In Situ Air Sparging, Chapter 3. Some key factors are discussed below.

b. **Respirometry Testing.** Site specific biodegradation potential may be evaluated by measuring respiration rates under controlled conditions (respirometry). A respiration test may entail measuring the rate of oxygen disappearance (utilization) as degradation proceeds. A biodegradation rate can then be estimated based on the uptake rate. Another variation uses the rate of evolution of carbon dioxide into the soil gas to perform a similar calculation. Both of these approaches must be evaluated with respect to abiotic sources and sinks for oxygen and carbon dioxide. In the oxygen uptake case, reduced iron may compete with microorganisms for oxygen. For carbon dioxide generation, inorganic carbonate dissolved in residual pore water and its precipitate may act as sources or sinks of carbon dioxide. Monitoring both oxygen uptake and carbon dioxide generation can help to clarify these confounding influences. Respirometry tests may be performed under laboratory conditions, but are best measured in situ, according to methods described in [EM 1110-1-4001](#) and AFCEE Principles and Practices of Bioventing (Leeson and Hinchee 1995).

c. **Microbial Enumeration Studies.**

(1) The presence of a high population density of microorganisms in contaminated soil is generally indicative of site conditions that have a relatively high biodegradation potential. However, a small population density of microorganisms does not necessarily indicate that biodegradation potential is low, but rather that existing conditions are not favorable for promoting microbial growth. If there are low microbial population densities, it is important to consider whether there are subsurface conditions limiting microbial activity that may be manipulated during remediation. For example, in soil contaminated with petroleum, the concentration of oxygen in the soil gas may be depleted (i.e., < 2%), and there may be relatively low population densities of aerobic heterotrophic (organic carbon metabolizing) microorganisms or aerobic contaminant-specific degrading microorganisms. However, upon exchanging the soil gas with ambient air containing >20% oxygen during MPE, population densities of aerobic microorganisms may increase rapidly and provide the means for biodegrading the petroleum contaminants. Similarly, soil lacking another limiting nutrient such as available nitrogen may have relatively low population densities of microorganisms but may be suitable for bioremediation if growth is stimulated through provision of this nutrient.

(2) Comparison of microbial population densities of background and contaminated zones provides additional insight into the feasibility of bioremediation. If there are significantly greater numbers of either heterotrophic or specific contaminant degraders present in the contaminated zone, then there is evidence that the microorganisms in the contaminated zone may be capable of biodegrading some (or all) of the contaminants. Again, the converse does not necessarily demonstrate that bioremediation is not feasible, but that there may be some factor inhibiting microbial growth.

d. **Bioavailability of Separate Phase Liquids.** Since microorganisms in the subsurface live in the aqueous phase (i.e., in pore water), (rather than within the NAPL), biodegradation of contaminants present in NAPL is not directly possible. The rate of biodegradation of the contaminants will generally be limited by the dissolution of the of the NAPL contaminants.

3-7. Checklist of Site Characterization Data. Table 3-10 lists data that should be obtained during site characterization for MPE or during pilot

testing. Items are prioritized so that the most necessary information is indicated by the most "+" marks. These priorities are common to most MPE sites, however, the practitioner must consider how these priorities apply to their specific site.

TABLE 3-10
Checklist of Site Characterization Data¹

Activity	Purpose	Reference
Soil Sampling +++	Determine physical and chemical soil characteristics	Paragraph 3-4 and 3-5 of this EM
Cleanup goals +++	Determine clean-up concentrations and time-frames	Paragraph 3-3 of this EM
Intrinsic permeability and air permeability of contaminated soils +++	Determine the potential rates of groundwater and soil gas recovery	Paragraph 3-4g(1) of this EM; USEPA 1995 Leeson et al. 1995
Soil structure and stratification +++	Determine how and where fluids will move within the soil matrix; identify possible permeability variations	Paragraph 3-4 of this EM USEPA 1995
Depth to groundwater +++	Difficult to apply MPE where the water table is less than 3 feet below grade. Some forms of MPE may not be possible where the water table is greater than 25 to 30 feet below grade (depending on elevation)	Paragraph 3-4e of this EM USEPA 1995 Kittel et al. 1994
Affinity of contaminants to soil +++	Contaminants with higher soil/water partitioning coefficients are harder to remove from soil	USEPA 1995; Paragraph 3-5c and 3-5e of this EM
NAPL source +++	Assess possible location(s) and estimate quantity	USEPA 1996b; Paragraphs 3-5a and 3-5b of this EM
LNAPL baildown test ++	Estimate recoverability of LNAPL in monitoring wells	Paragraph 3-5a(3) of this EM Leeson et al. 1995
In-situ respirometry test ++ ²	Evaluate in-situ microbial activity	Paragraph 3-6b of this EM Leeson et al. 1995
Volatility of constituents ++	Determine the rate and degree of contaminant vaporization; estimate initial levels of VOCs in extracted gas	USEPA 1995 EM 1110-1-4001
Moisture content of unsaturated zone ++	Moisture content reduces air permeability	Paragraph 3-4d of this EM USEPA 1995
NAPL analysis ++	Physical and chemical composition of NAPL	Paragraphs 3-5a(7) and 3-5b(2) of this EM
pH of soil and groundwater +	Determine conditions for biodegradation	Paragraphs 3-5c and 3-5e of this EM
Nutrient (e.g., nitrogen, phosphorus) concentrations in soil and groundwater +	Determine conditions for biodegradation	Paragraphs 3-5c and 3-5e of this EM
Metals concentrations in soil and groundwater +	May be toxic to microbes. Metal in groundwater must be considered for design of treatment systems.	Paragraphs 3-5c and 3-5e of this EM
¹ Importance of data for technology screening indicated by number of plusses, +++ most important. ² May not be important or cost-effective at sites where biodegradation is not expected to contribute significantly to mass removal. For example, sites with compounds that are not amenable to aerobic biodegradation such as PCE or heavy fuel oils; or sites where LNAPL removal is the important remedial goal.		

3-8. Remedial Technology Options. This section describes a range of MPE options and related technologies that may be considered during the technology screening process. These include single- and multi-phase non-vacuum-enhanced and vacuum-enhanced extraction technologies, as well as alternatives to these technologies (e.g., excavation) and ancillary technologies (e.g., soil fracturing) that can be used in conjunction with MPE technologies. Site-specific considerations such as soil characteristics, initial and required contaminant concentrations, and depth to groundwater will determine which technology or group of technologies will be optimal for a given situation.

a. **Excavation.** Excavation is a remedial option for shallow contaminated soils that may not be easily treated by in-situ methods. It is usually limited to the operating depth of the excavation equipment and to volumes of soil small enough that normal site operations are not interrupted (API 1996). The cost of excavation and disposal is often used as a baseline against which the costs of other technologies are compared. When excavation is performed, depth to groundwater is an important factor. Once excavation approaches the groundwater table, dewatering of the excavation is usually necessary and methods to keep the excavation from collapsing from infiltrating groundwater (e.g., slurry walls) may be necessary. Shoring of excavation walls may also be required in non-cohesive, more permeable soils. Excavated soil can be treated on site (e.g., treating soil piles via SVE [EM 1110-1-4001]) or disposed of off-site.

b. **Conventional LNAPL Recovery.** Conventional LNAPL recovery uses an electric or pneumatic pump to remove LNAPL from the surface of the water table. This is accomplished using a skimmer pump for LNAPL-only recovery, a dual pump system utilizing a submersible pump for water table depression with a skimmer pump for LNAPL removal, or a total fluids pump which removes LNAPL and water together and separates the two liquids aboveground. Conventional LNAPL recovery is best suited for sites with homogeneous, coarse-grained soils that will allow LNAPL to flow freely into a recovery well or trench. Table 3-11 lists advantages and disadvantages of various types of conventional LNAPL recovery systems, and Table 3-12 lists the most suitable method based on recovery flow rates.

TABLE 3-11

Advantages and Disadvantages of Conventional Liquid Hydrocarbon Recovery Systems

Trenches and Drains	Skimming Pump Wells	Single Pump Wells	Dual Pump Wells
Advantages			
<ul style="list-style-type: none"> • Simple operation and maintenance • Materials and equipment are available locally • Quick, cost-effective installations are possible if soil conditions are favorable • Complete plume interception 	<ul style="list-style-type: none"> • Little or no water is produced • Simple operation and maintenance • Inexpensive 	<ul style="list-style-type: none"> • Simple to operate • Inexpensive and reliable • Low operating and maintenance costs • Create capture zones 	<ul style="list-style-type: none"> • Separation of the product and water within the well • Decreased soluble components in the produced water • Allows highest degree of automation to maximize the rate of recovery • Create capture zones

TABLE 3-11 (Continued)

Trenches and Drains	Skimming Pump Wells	Single Pump Wells	Dual Pump Wells
Disadvantages			
<ul style="list-style-type: none"> The entire width of the migrating plume must be bisected unless water depression is used to capture the LNAPL plume Depth limited by soil conditions, equipment, soil disposal considerations, and cost Construction is difficult in congested areas Contaminated soil disposal 	<ul style="list-style-type: none"> Small area of influence Lack of hydraulic control 	<ul style="list-style-type: none"> Need for aboveground hydrocarbon/water separation system Tendency to emulsify the hydrocarbon and water The dissolved components in the produced groundwater are increased Creates additional smear zone in the cone of depression 	<ul style="list-style-type: none"> Higher capital, operating, and maintenance costs Initial start-up and adjustments require experienced personnel Applicability to low transmissivity formations is questionable Larger volumes of extracted water require treatment and disposal Creates additional smear zone in the cone of depression
After API 1989. Reprinted by permission of American Petroleum Institute. Copyright 1989. All rights reserved.			

TABLE 3-12

LNAPL Pumping System Versus Recommended Operational Range

Pump Type	Liquid Production Rate Per Well		
	Low <20 lpm (<5 gpm)	Medium 20-75 lpm (5-20 gpm)	High >75 lpm (>20 gpm)
Skimming			
Down hole	_____		
Suction lift	_____		
Vacuum-enhanced (MPE)			
Shallow	_____		
Deep	_____		
Pneumatic single pump			
Submersible	_____		
Suction lift	_____		
Electric single pump			
Submersible	_____		
Suction lift	_____		
Two-pump systems			
Submersible electric		_____	
Submersible pneumatic		_____	
Suction lift		_____	
Note: lpm = liters per minute; gpm = gallons per minute			
After API 1989. Reprinted by permission of American Petroleum Institute. Copyright 1989. All rights reserved			

(1) Trench/Drain Systems. A trench/drain system involves installation of a permeable trench to recover LNAPL. A trench is installed with very permeable backfill (e.g., gravel), and sumps or wells are installed within the trench. This allows LNAPL to flow more freely from the formation into the permeable trench, and into the sump(s). LNAPL is then recovered from the sump(s) by one of the methods discussed in 3-8b(3) and 3-8b(4). Trenches are usually installed downgradient of a LNAPL plume and may include an impermeable layer on the downgradient side of the trench to prevent LNAPL migration beyond it (API

1996). They must be excavated several feet below the lowest seasonal water table elevation (API 1996). Figure 3-6 illustrates a typical trench and drain system.

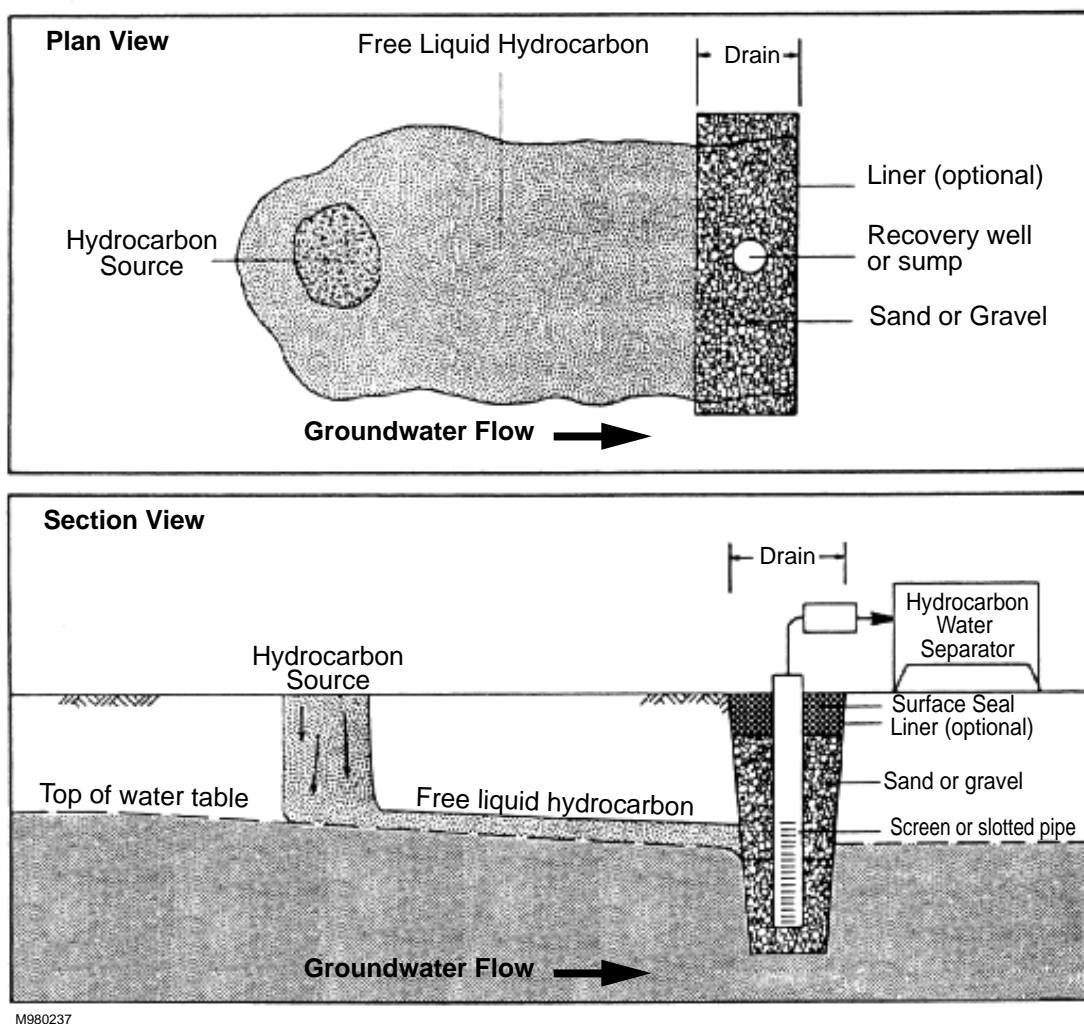


Figure 3-6. Trench and Drain LNAPL Recovery System. (API 1996. Reprinted by permission of American Petroleum Institute. Copyright 1996. All rights reserved.)

(2) Recovery Wells. Another method of LNAPL recovery is via recovery wells. Recovery wells are of large enough diameter to accommodate a LNAPL recovery pump. Wells typically do not recover LNAPL at rates as high as trench/drain systems because they do not influence as large an area. Wells do, however, offer more flexibility in design, placement, and operation than a trench and drain system (API 1996).

(3) Skimming. Skimming involves removal of LNAPL only that drains from the formation into a recovery well or trench/drain system. Skimming systems rely on passive movement of LNAPL into the product recovery system and

therefore have a very small radius of influence outside of the well or trench (Leeson et al. 1995).

(4) Drawdown. LNAPL recovery by drawdown can be performed using a single total fluids pump or separate groundwater and LNAPL recovery pumps. Single pump systems are installed below the water table and extract groundwater and LNAPL in the same stream that is then separated aboveground. Dual pump systems use a submersible water pump to lower the groundwater table and an LNAPL skimming pump to recover LNAPL that migrates into the well. Drawdown systems for LNAPL increase recovery by depressing the groundwater table, which induces a gravity gradient for LNAPL to flow into the collection system (Lesson et al. 1995). Drawdown can, however, result in entrapment of LNAPL within the cone of depression, potentially deepening the smear zone of LNAPL in the soil, which can be difficult to remediate (Leeson et al. 1995). Figure 2-6b illustrates a dual pump system for LNAPL recovery.

c. Vacuum Dewatering. Dewatering has long been a technique used in the construction industry to prevent water exfiltration from the soil into excavations and to stabilize soils to prevent excavation slopes from collapsing. Silt and clay excavations often have very unstable slopes and sidewalls (Powers 1992). Unstable silts can "act as a liquid" and destabilize the lateral loads on sheet piles, causing bracing failures (Powers 1992), particularly when subjected to aboveground compression from heavy construction equipment. Since silts and clays typically produce relatively low water flow rates when relying solely on gravity drainage, vacuum dewatering using closely spaced well points is common. Vacuum dewatering well points typically produce higher (though still low) water flow rates that can dramatically increase the stability of excavation side walls. Powers (1992) reports that this beneficial effect is observed even in sediments where the reduction in moisture content due to vacuum dewatering is small. Vacuum dewatering is typically achieved using driven well points that are sealed at the ground surface to ensure that the vacuum is transmitted to the soil. Vacuum is applied to the well points either using oil-sealed or water-sealed rotary vane or liquid ring pumps. Use of these pumps may be hampered by the limit of vacuum lift, e.g., 30 feet (9.1 m) of water. Ejector pumps (sometimes referred to as jet pumps) are commonly applied for construction dewatering at depths deeper than 28 feet (8.5 m). Powers (1992) is an excellent resource for additional information about excavation dewatering techniques and common practice.

d. Vacuum-Enhanced LNAPL Recovery. MPE has evolved as a remediation method that applies the technology pioneered for construction vacuum dewatering to enhance the recovery of LNAPL. At many sites, LNAPL present in the capillary fringe can not flow toward extraction wells due to capillary forces holding the LNAPL within soil pores (Baker and Bierschenk 1995). This phenomenon is common in fine-textured soils such as fine sands, silts and clays. By applying high vacuums at extraction wells, the capillary forces holding the LNAPL in the soil can to some degree be overcome and LNAPL can flow toward the extraction well. This technique can be implemented in two ways: MPE without drawdown of the surrounding water table (analogous to LNAPL skimming) and MPE with drawdown (analogous to LNAPL recovery using dual pumps). These techniques are discussed below.

(1) MPE Without Drawdown.

(a) MPE without drawdown is often conceived of as similar to free-product skimming with the addition of vacuum applied at the extraction well to induce LNAPL to migrate toward the well. Under these circumstances, the vacuum is typically applied at the water table surface where the LNAPL resides, and the LNAPL is induced to travel horizontally toward the MPE well. This process can

be implemented by either applying a vacuum to the top of a sealed conventional well containing a skimming pump or using a drop tube to apply the vacuum and extract the LNAPL.

(b) This common conceptualization of MPE without drawdown must be modified to account for upwelling of liquid in and around the extraction well. As described previously, application of a vacuum to an extraction well initiates a complex response of water, LNAPL, and air around the well. However, the influence of the applied vacuum in the formation outside of the immediate well area can induce LNAPL to migrate toward the well and eventually flow into the well. If a skimmer is used for product recovery and the vacuum is applied at the well head by a separate piping system, then there may not be an increase in subsurface vacuum. Because upwelling can offset the air vacuum gradient created by the extraction of air, the benefit of such a configuration is limited to overcoming the capillary pressure preventing the product from entering the filter pack.

(c) Unlike conventional LNAPL skimming, MPE without drawdown typically extracts significant quantities of water along with air and LNAPL from the subsurface. Therefore, in addition to LNAPL collection, the water and air streams must also be managed and treated.

(2) MPE with Drawdown. The use of MPE with drawdown is a means of increasing NAPL recovery. It also dewateres the zone below the water table in an area around the well, exposing residual NAPL in that zone to the air phase.

(a) MPE with drawdown is simply a vacuum-enhanced version of conventional LNAPL recovery with drawdown. When a vacuum is applied to a conventional LNAPL recovery with drawdown system, the imposed vacuum gradient provides a force in addition to the gravitational force inducing LNAPL to flow toward the extraction well. The applied vacuum induces greater water (and NAPL) flow to the well than can be achieved under typical drawdown conditions. This process can also be employed using a drop tube placed below the water table, extracting water, LNAPL, and air all through the same tube. (Using a drop tube instead of a downhole dual-pump or total fluids pumping system involves other complications regarding the dynamics of liquid and droplet flow in pipes as described in [paragraph 2-5d.](#))

(b) As in MPE without drawdown, MPE with drawdown will generate groundwater, air and LNAPL to be managed and treated aboveground. MPE with drawdown will typically result in more groundwater extraction from a given well than MPE without drawdown. However, the most commonly perceived benefit of using this technique is to dewater the soil surrounding the MPE well to expose to air discontinuous ganglia of LNAPL trapped below the water table. As the water table is drawn down, these ganglia may either drain toward the declining water table surface due to gravity and vacuum inducement, or they may volatilize and be extracted in gas that flows to the MPE well.

e. Multiphase Extraction to Enhance SVE/BV. MPE is generally accomplished using two distinct technologies. Dual-phase extraction (DPE) technology generally employs separate pumps to extract liquid and gas from a well. Two-phase extraction (TPE) extracts liquid and gas from a well using a single suction pipe or conduit. These technologies are discussed below.

(1) Dual-Phase Extraction.

(a) DPE systems typically use a submersible or pneumatic pump to extract ground water, and a low vacuum (approximately 76 to 305 mm Hg, or 3 to 12

inches Hg) or a high vacuum (approximately 457 to 660 mm Hg, or 18 to 26 inches Hg) blower to extract soil gas (USEPA 1997a; Zahiraleslamzadeh 1998). A typical DPE system is shown in Figure 3-7. DPE can be used to perform MPE either with or without drawdown. The amount of drawdown is determined by setting the intake of the pump or the level controls.

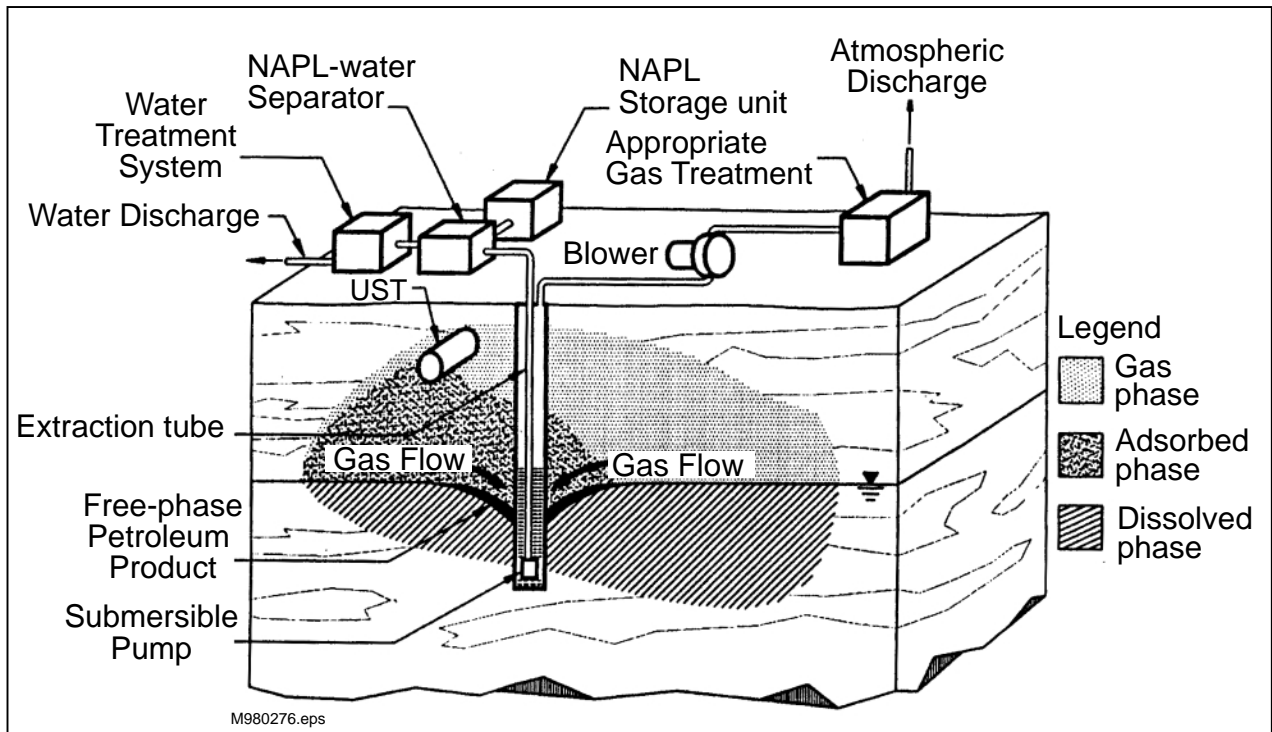


Figure 3-7. Typical Dual-Phase Extraction System. (After USEPA 1995)

(b) A key attribute of the DPE technology is that liquids and gas are withdrawn from the extraction well via separate conduits, allowing independent measurement and control of the flows of each fluid. Such independent measurement and control of the fluid flow are not readily accomplished with TPE, which can be particularly important in a multi-well system, where several wells are connected to the same blower or pump via a common manifold.

(2) Two-Phase Extraction.

(a) TPE is characterized by extraction of liquids and air from a well using a single suction pipe (Figure 3-8). TPE employs a high vacuum (approximately 457 to 660 mm Hg, or 18 to 26 inches Hg) pump to extract total fluids from an extraction well (USEPA 1997a). A suction pipe (often called a drop tube or a slurp tube) is lowered into the extraction well to a predetermined depth to accomplish MPE either with or without drawdown. MPE capital costs are reduced by using a single pumping system.

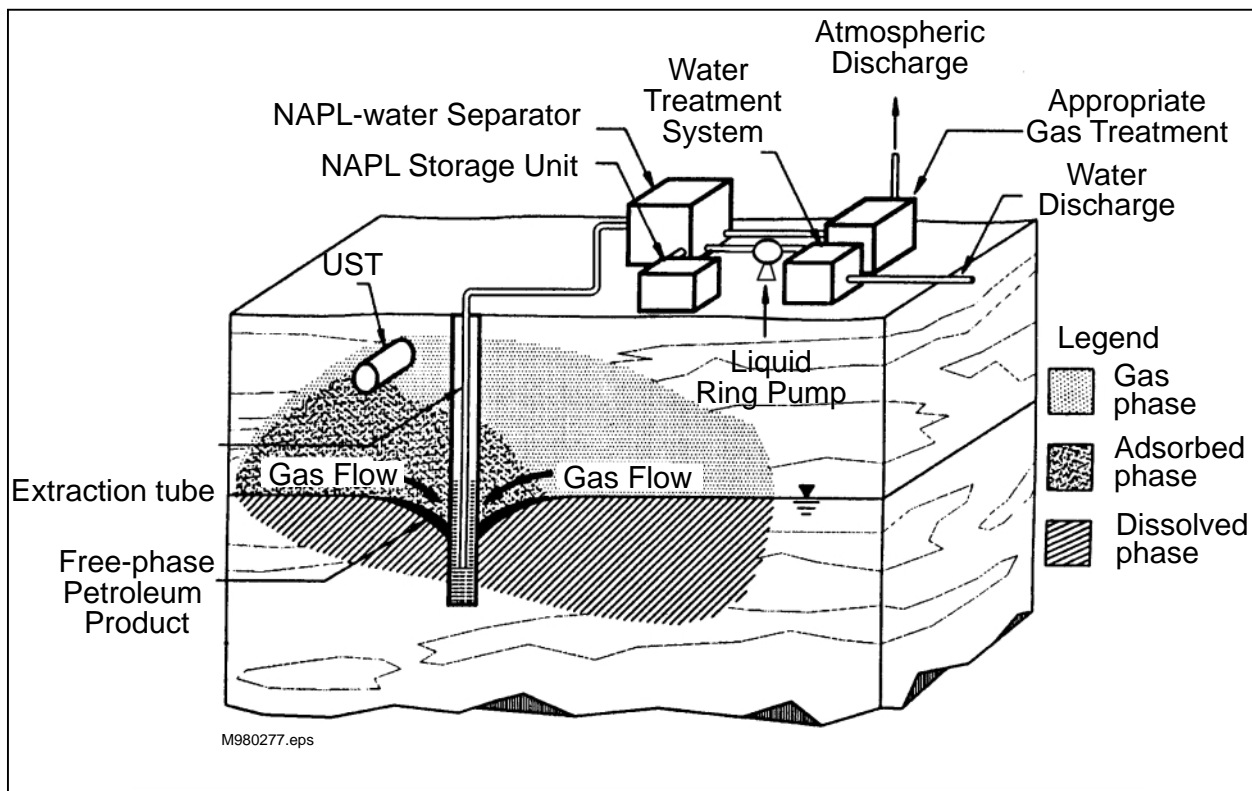


Figure 3-8. Typical Two-Phase Extraction System. (After USEPA 1995)

(b) Liquid lift via the TPE method is accomplished either by direct vacuum lift (i.e., where one inch of water vacuum raises the water level by one inch), or at depths greater than 9.1 m (the limit of suction lift of water, Powers 1992), by entraining liquid droplets in air and removing both phases together simultaneously from the well. Turbulence in the suction pipe may cause these droplets to hit the sides of the pipe. In this case, the liquid forms a layer on the inside of the pipe that is forced up the well by the velocity of the air inside the pipe. Under these conditions, the effective extraction depth can be much greater than 9.1 m (30 feet) as long as the air velocity in the pipe is sufficient to force the liquid up the pipe. There are differing opinions regarding the air velocity necessary to aspirate liquids from a well. Mickelson (1994) recommends linear air velocities in excess of 914 m/min (3,000 ft/min). AFCEE has reported velocities as low as 275 m/min (Kittel et al. 1995). A velocity of 500 m/min can be assumed for most TPE applications. It may be necessary to consider patent issues associated with TPE ([see paragraph 9-3](#)).

(3) DPE and TPE Considerations.

(a) Liquid and gas flow from extraction wells can be measured and controlled more effectively in DPE systems compared to TPE systems. Therefore, DPE provides more opportunity for developing a system in which flow rates from the MPE wells in a network can be balanced to accommodate differences in soil characteristics across the treatment area. A common problem with TPE systems is breaking suction at one or more of the wells in the network. If a single well is able to produce a high flow rate of air, then the vacuum in the entire

system can be reduced to a level that is insufficient for liquid extraction at other wells. This phenomenon is shown in Figure 3-9. As shown in this figure, there typically is little advance indication that a break in suction is about to occur. While the gas (and liquid) flows from each well are apt to differ (due to variability in subsurface properties), the vacuums being applied to each well are typically set at similar levels to balance the system. When more air enters one of the wells, which can occur if the soil is more permeable at some locations than at others (as is often the case), then the TPE system short-circuits and both the applied vacuum and flows greatly diminish at the other, non-breaking wells.

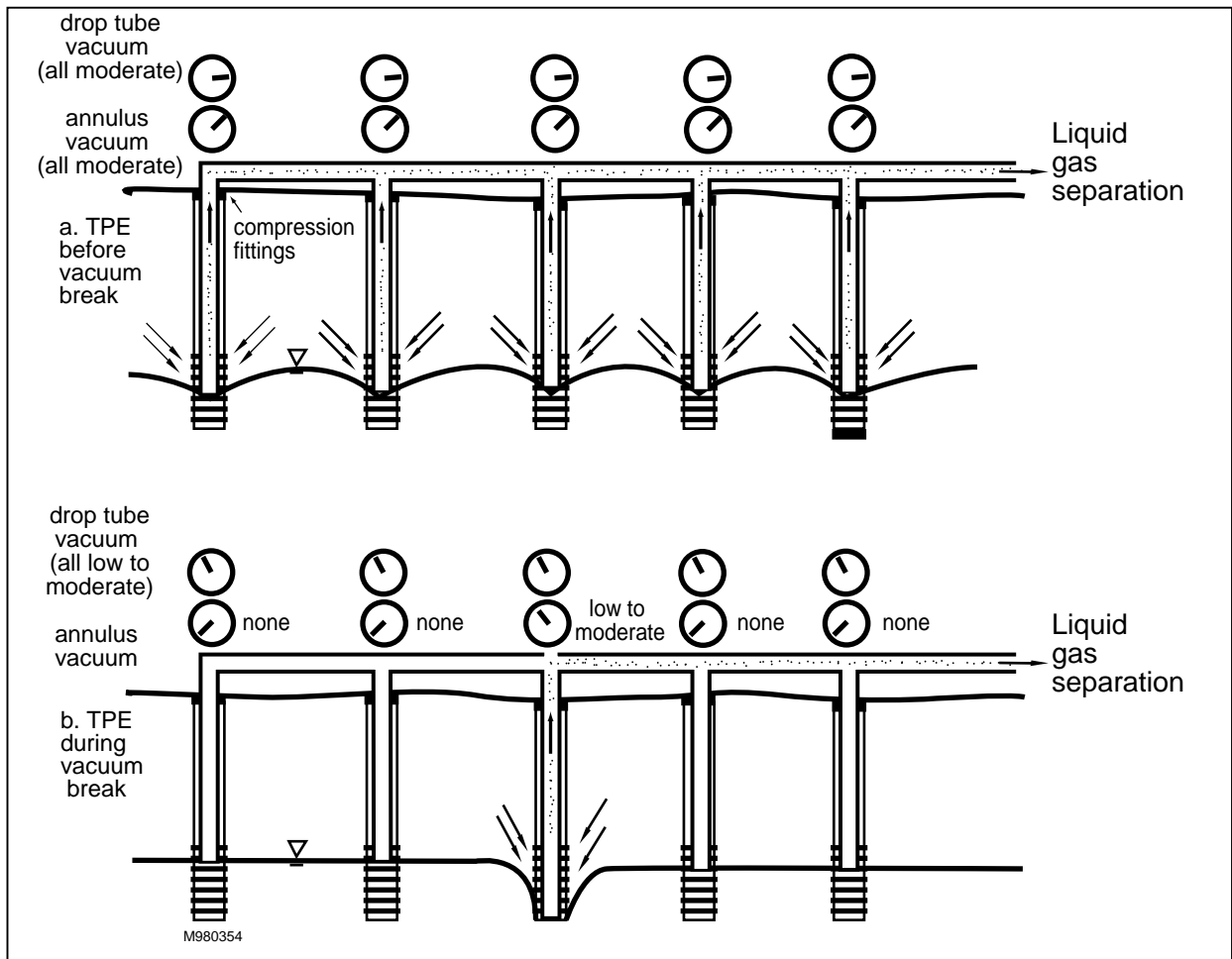


Figure 3-9. Two-Phase Extraction (a) Before and (b) During Vacuum Breaks.

(b) This effect of breaking suction is minimized or eliminated in a DPE system, since the flow rates of gas and liquid can be monitored and controlled separately. Suction break is controlled in the liquid pump with level sensors that shut down the pump when the water level approaches the intake. With DPE, monitoring of individual well gas flows permits advance warning that suction may be about to break, and allows provision of a feedback system to reduce the

flow from the problem well or wells. Thus, suction breaks are preventable, resulting in better control, less downtime, and more efficient operation for heterogeneous, multi-well sites.

(c) However, this degree of control comes at an increased capital cost for comparable DPE versus TPE systems. Liquid pumping systems in soils that require high vacuums can be quite expensive. The selection of a liquid pumping system for DPE will depend upon the depth to the water table. For depths greater than 9.1 m, submersible pumps are typically used to evacuate liquids from the extraction wells. In low permeability soils, more costly pneumatic pumps may be required.

f. Vacuum-Enhanced Groundwater Pump and Treat.

(1) Vacuum-enhanced pump and treat may be used to increase the groundwater capture zone of a pumping well beyond that which can be achieved by groundwater pumping alone. Because the discharge that can be obtained is proportional to the capture zone (that zone within the cone of depression), this method increases the rate of groundwater withdrawal from an individual well. This method thus can decrease the number of wells that are needed. The method is a type of MPE, the differentiating factor being that in this case groundwater is the target, and the aim is to withdraw as much groundwater as possible. This method is applicable in situations where transmissivity is low due to small saturated thickness and/or relatively low permeability (in the range of 10^{-3} to 10^{-5} cm/sec).

(2) As in other types of MPE, a single- or dual-pump system is used. A single-pump (TPE) system utilizes one pump to extract liquid and gas via a drop tube. This type of system is not usually a cost-effective means of enhancing groundwater recovery.

(3) A dual-pump system (DPE) uses separate liquid and gas pumps. A vacuum is applied at the well head, while a second downhole pump is used to withdraw liquids.

g. DNAPL Recovery.

(1) At some sites, the physical/chemical properties of the DNAPL combined with the release history and geologic conditions result in the formation of zones of potentially mobile DNAPL (e.g., pools). When mobile DNAPL is encountered, there are a number of methods and designs that can be employed to ensure optimal recovery efficiency. Under the most favorable conditions, direct recovery will remove between 50 and 70 percent of the DNAPL in the subsurface (Pankow and Cherry 1996). The remaining residual DNAPL will still be sufficient to serve as a significant long-term source unless it is addressed through other means.

(2) In order to properly design DNAPL recovery systems, it is important to know where the mobile DNAPL is located in the subsurface. In unconsolidated deposits, sufficient geologic information must be obtained to delineate the stratigraphy, map the extent of the DNAPL (from the "outside-in", if possible), and identify the extent and orientation of the low permeability, fine-grained deposits that may be trapping the DNAPL. These data can be obtained quickly and cheaply using direct-push drilling methods to collect continuous soil cores (paragraph 3-4h(2)). It is important to carefully screen and inspect the cores to determine the locations of the mobile DNAPL zones and the controlling stratigraphic zones. In some cases, the bedrock surface underlying the unconsolidated deposits may act as a confining layer and result in the

formation of mobile DNAPL at the bedrock-soil interface. In these situations, non-invasive geophysical methods may be used to attempt to delineate the topography of the bedrock surface and identify low points where DNAPL may be trapped.

(3) Once the mobile DNAPL zone(s) are identified, the extraction system can be designed. The screen interval of DNAPL recovery wells should correspond to the subsurface zone containing the DNAPL. At sites where several zones are encountered at different elevations, it is advisable to begin extracting from the upper-most zone first and then extracting from progressively lower zones once the upper zone(s) have ceased DNAPL production. This will maximize recovery efficiency and minimize the potential for uncontrolled mobilization.

(4) Creating a shallow sump in a less permeable stratum at the bottom of the well for the collection of the DNAPL may also be advisable. The sump will provide a convenient and efficient location for placing the intake of the DNAPL pump (Michalski et al. 1995).

(5) A total liquids approach can be used (i.e., water and DNAPL are removed from the well via one pump and then separated at the surface). This may minimize equipment costs; however, it is not the most efficient approach. As the DNAPL and water are extracted from the well, the DNAPL saturation is decreased in a zone around the well, the relative permeability of the formation with respect to DNAPL is decreased, and the DNAPL production rate decreases. Eventually, a zone of residual (non-mobile) DNAPL is created around the well and the well no longer produces DNAPL.

(6) The ideal approach is to maintain or enhance DNAPL saturation around the well in order to increase removal efficiency. DNAPL extraction can be enhanced using a dual pumping approach, where water is removed separately from the zone immediately above the mobile DNAPL (Sale and Applegate 1997). This approach results in upwelling of DNAPL in the well, and increased DNAPL saturations in the immediate vicinity of the well. A variation of this approach is to apply a vacuum to the upper of the two wells, to decrease the pressure head in the well. This has a similar effect as pumping water, in that it results in a decrease in the total head in the well (i.e., increased hydraulic gradients near the well) and increased DNAPL thicknesses, saturations, production rates, and removal efficiencies.

h. Ancillary Technologies.

(1) Soil Fracturing.

(a) Soil fracturing is a technique that may enhance the effectiveness of MPE remediation systems. The essence of this enhancement is the creation of additional high permeability pathways within otherwise low permeability strata to extend the influence of MPE wells. Soil fracturing can be accomplished either pneumatically (i.e., by injecting air at high pressure) or hydraulically (i.e., by injecting water, or a slurry of water and sand and/or gel) into the soil to create fractures or channels. Fractures are created in boreholes by injecting the air or water slurry at high pressure at intervals along the depth of the boring. A typical application may develop fractures approximately 0.5 to 1 cm wide (pneumatic) or 1 to 2 cm wide (hydraulic) at 2 foot (60 cm) intervals along the borehole. The fractures typically form horizontally away from the borehole (though they may propagate vertically as well), in a radius of 10 to 60 feet from the borehole (USEPA 1997a). The soil hydraulic fracturing often includes injection of material such as sand and gel (e.g.,

guar gum) to keep the fractures open (often described as "propped open"). In contrast, pneumatically created fractures may close somewhat over time.

(b) The new network of fractures increases the surface area of soil affected by the vacuum subsequently applied at the MPE well. In this way, soil fracturing has the potential for increasing the zone of influence of an MPE well. However, the effectiveness of soil fractures will depend upon the remediation objectives of the MPE system. Soil fracturing will increase the flow of air and liquids into MPE wells, and therefore can increase the rate of mass removal from the subsurface. If mass removal is the primary objective, then soil fracturing can be a useful enhancement. However, if a MPE system is intended to extract the contamination that resides within the low permeability soil matrix (e.g. if soil concentrations must be reduced to a specified level), diffusion limitations may still prevail even after soil fractures are developed. Murdoch (1995) and Shuring (1995) provide further information regarding the applicability and performance of soil fracturing.

(2) Air Injection. As described in Chapter 3 of [EM 1110-1-4001](#), air injection into the vadose zone is a useful enhancement of the SVE process. Air injection into the vadose zone can accomplish several purposes:

(a) It can increase the effectiveness of SVE by increasing subsurface pressure gradients, thereby increasing subsurface gas flow rates. Airflow to a SVE well is generally a function of the soil permeability and the subsurface pressure gradient. If SVE is achieved through extraction alone, then the maximum pressure gradient is between essentially atmospheric pressure and the SVE well vacuum. If air is injected at a substantial pressure, then the pressure gradient increases and airflow rates increase proportionally.

(b) In addition, air injection within a multi-well MPE wellfield can help eliminate stagnation zones that may develop where multiple MPE wells "negate" each other's influence. This effect is depicted in Chapter 5 of [EM 1110-1-4001](#).

(c) Air injection is also one of the primary methods of implementing bioventing within the vadose zone. Biodegradation of vadose zone contaminants is often oxygen-limited. Air injection is the preferred method of supplying oxygen, since this method does not require extraction and treatment of contaminated air aboveground.

(3) Air Sparging. Airsparging is a technology for remediation of in-situ soil and groundwater. It involves injection of air below the water table, which causes dissolved volatile contaminants to partition to the gas phase for subsequent extraction in the vadose zone via soil vapor extraction. Air sparging also provides oxygen to groundwater and soil, promoting aerobic biodegradation of contaminants. [EM1110-1-4005](#) In-Situ Air Sparging provides guidance on this technology.

(4) Surfactant/Cosolvent Flushing.

(a) Surfactant or cosolvent flushing is an emerging technology for increasing the effectiveness of groundwater extraction and MPE systems. The premise of this technology is that most organic NAPL is only sparingly soluble in water and therefore will persist in the subsurface for a very long time. However, chemical amendments to the groundwater can cause many types of NAPL to dissolve in the groundwater much more readily. Cosolvents such as alcohols, or surfactants such as detergents can, when added to the groundwater in high concentrations (e.g., 50% by volume in the case of cosolvents), enhance the

rate of NAPL dissolution by orders of magnitude. In this way, a MPE system that would require extraction of thousands of pore volumes to "flush" residual NAPL from the saturated zone by groundwater dissolution and extraction alone might require extraction of tens or hundreds of pore volumes of chemically amended water.

(b) Implementation of surfactant or cosolvent flushing involves installation of injection wells to introduce the chemical amendment into the contaminated zone. Groundwater is typically recirculated through the contaminated zone in an effort to achieve the widest possible dispersion of the additive throughout the contaminated area. While this technology is quite promising, it is also relatively expensive. This approach suffers from the same limitations as MPE in heterogeneous unsaturated soils; that is, the tendency of the surfactant/cosolvent laden water to preferentially flow through the highest permeability strata, which may not be where the bulk of the contaminant mass resides.

(c) Great care must be exercised when injecting surfactants or other chemicals into the subsurface. The risk of mobilizing contaminants in the absence of adequate hydraulic control is significant with these technologies. For this reason, regulators are often wary of approving remediation plans involving the injection of chemicals such as surfactants.

(d) The AATDF Technology Practices Manual for Surfactants and Cosolvents (TR-97-2, available on the internet at www.clu-in.org/PRODUCTS/AATDF/Toc.htm), produced by the DOD Advanced Applied Technology Demonstration Facility Program at Rice University, provides further information regarding evaluation and potential application of surfactant/cosolvent flushing for remediation of subsurface contamination. The report provides a basic understanding of the technologies, their applicability and limitations, and an understanding of the factors to be considered when implementing projects.

(5) Groundwater Pump-and-Treat.

(a) Groundwater pump-and-treat is the process of removing contaminated groundwater via recovery wells and pumping it to the surface for treatment. Pump and treat is primarily used as a technology for plume containment. Extracted groundwater is treated by one of several methods based on its contaminant concentration and contaminant properties. In most hazardous waste site pump-and-treat systems, groundwater is treated by air stripping (for volatile contaminants), ultraviolet oxidation, and/or carbon adsorption (for removal of additional contaminants or polishing). Pump-and-treat may be a viable option to keep contaminated groundwater from migrating off site or to enhance recovery of contaminants in the capillary fringe when operating concurrent with soil vapor extraction. As the sole remediation process, however, pump-and-treat can take a very long time to clean up a site. This is because it will only recover dissolved contaminants within the groundwater and will not remediate residual contaminant or treat the source of the contamination. MPE can be used to replace pump-and-treat, particularly at sites with low transmissivities. More information on groundwater pump-and-treat can be found in USEPA 1990, Basics of Pump-and-Treat Ground-Water Remediation Technology; NRC (1994); and other USACE guidance on groundwater extraction lessons learned.

(6) Thermal Enhancements.

(a) There are a number of methods that can be used to inject or apply heat to the subsurface to enhance MPE. Thermal enhancement is used to lower the

viscosity of NAPL, increase the vapor pressure and solubility of VOCs or SVOCs to enhance their removal, and/or increase air permeability by removing soil moisture.

(b) Steam injection may displace mobile contaminants, pushing them ahead of the condensing water vapor ("steam front") toward extraction wells, as well as vaporize residual volatile constituents. Thus, contaminants can be recovered in both the liquid and gas phases. Steam may be injected above or below the water table.

(c) Electrical energy may be applied to soil in the low frequency range used for electrical power (electromagnetic, alternating current, or resistivity heating) or in the radio frequency (RF) range. For low frequency range heating, the boiling point of water (100°C) is the highest temperature that can be achieved. RF heating can achieve higher temperatures of up to 300° or 400° C. However, RF is only about 40% efficient in producing heat from electrical energy.

(d) Thermal conduction heating, or "in-situ thermal desorption," relies on conduction rather than convection to heat subsurface soils. For shallow soil contamination, surface heater blankets may be used. For deeper soil contamination, heater wells are used. Most contaminants are destroyed in situ, while the remainder volatilize, and are removed by vacuum and treated aboveground using VOC emission control equipment.

i. Examples of Integrated Technologies. Given the nature of subsurface contamination, it is common to apply more than one technology to remediate a site. For example, it is common to have both groundwater and vadose zone contamination at the same site. MPE may be integrated with several of the ancillary technologies described above. Many of these technologies include extraction as part of the process. In medium and low permeability soils (i.e., $< 10^{-4}$ cm/sec hydraulic conductivity), extraction will best be performed using an MPE-type system. For example, extraction in a cosolvent flushing system in 10^{-4} cm/sec sands can be performed using MPE. Similarly, gases generated using high temperature thermal desorption technology, along with excess water, can be captured using MPE technology in fine-grained soils.

3-9. Feasibility Studies for MPE.

a. The Feasibility Study (FS) is a combination of the physical, chemical and biological evaluations described in the previous sections, paired with an evaluation of the potential remedial approach(es). Nine evaluation criteria are specified for feasibility studies for CERCLA sites (USEPA 1988). Similar criteria are specified for RCRA Corrective Measures Studies. In addition, many states have adopted some or all of these criteria for feasibility studies under state regulatory programs. The criteria are: 1) overall protection of human health and the environment, 2) compliance with applicable or relevant and appropriate requirements (ARARs), 3) long-term effectiveness and permanence, 4) reduction of toxicity, mobility, and volume through treatment, 5) short-term effectiveness, 6) implementability, 7) cost, 8) state acceptance, and 9) community acceptance.

b. The practitioner must consider a variety of technologies before selecting a remediation approach. Figure 3-1 provides a decision tree for evaluating the technical applicability of MPE, i.e., whether, in one of its various forms, MPE is appropriate for a given site. Use of this decision tree requires site-specific values for each of the parameters/criteria referenced in the decision tree.

c. A part of the feasibility study is an economic evaluation of the likely cost to test and implement MPE, in comparison to other technologies. Many feasibility studies recommend the technology that is likely to attain cleanup goals for the site at minimum cost. For an in situ technology such as MPE, this cost of treatment is very site-specific, and is primarily affected by the concentration and mass of extracted hydrocarbon that must be treated and site stratigraphy and permeability. Cost estimates for each of the alternatives must include treatment of all of the extracted waste streams (NAPL, water, and air). Other important cost considerations include the number of wells that are required to achieve sufficient air and liquid flow in the treatment zone; the complexity of the system, which dictates the O&M level of effort; and the projected time of treatment required.

d. An FS report is usually prepared in which potential remedial technologies are identified and evaluated against the required criteria. The FS will generally lead to a site-specific MPE pilot test if the technology still appears promising. Alternatively, pilot testing may be performed as part of the FS. Laboratory tests may also be performed, for example, laboratory column studies simulating airflow in soil may be informative (e.g., Ji et al. 1993). The use of laboratory scale testing for technology assessment should be cautiously approached as scaling and sizing issues may be left unresolved. Pilot test methods and guidance will be provided in the next chapter.